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THE USE OF THE HALOCHROMIC EFFECT IN QUANTITATIVE CHEMICAL ANALYSIS*

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Saratov State Teaching Institute

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Original article submitted November 27, 1959

The halochromic effect, i.e., the formation of intensely colored addition products by many organic compounds of the strong acids H_2SO_4, $HClO_4$, or inorganic compounds of the type $SnCl_4$, $AlCl_3$, $SbCl_3$, etc. has been studied by many authors [1-3]. The mechanism of these reactions reduces to an acid-base interaction of an organic dye with an inorganic reagent. Molecular compounds are formed by all organic reagents which contain the atomic groupings: $>C=O$, $-N=O$, $-N=N-$, $>C=N$, $>C=C<$, etc. having readily mobile π-electrons. The combination of the groups indicated with a system of aromatic type conjugated bonds, as well as the possibility of a change over into an ionic state, leads to the development of intense absorption bands in the visible part of the spectrum [4-6].

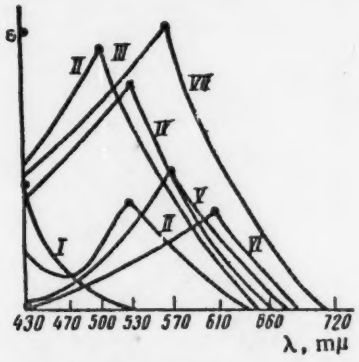


Fig. 1. Absorption curves of the halochromic compounds formed by dyes I-VII (Table 1) in H_2SO_4.

Some reactions in which halochromic compounds are formed have found analytical application, e.g., the method for the quantitative determination of $SnCl_2$ developed by Alimarin and Pevzner [7], the detection of carotene with concentrated sulfuric acid, the detection and semiquantitative determination of antimony with thymolphthalein [8], titration of hypochlorites in an acid medium by means of methyl orange [9], etc. Since, however, the appropriate reactions have not been studied sufficiently, the halochromic effect has not found wide application in quantitative inorganic analysis.

The present article is devoted to showing the possibility of using the halochromic compounds formed by dyes, as reagents for the quantitative determination of a number of oxidizing agents. In addition to dyes containing the atomic group $-N=N-$, it may be possible to use other dyes with different characteristic groups in chemical analysis.

In Fig. 1 are shown the absorption curves of the halochromic compounds of several azo dyes, while in Table 1 are given the values of the molar absorption coefficients of a number of azo dyes, their solubility in H_2SO_4, and their behavior toward certain oxidizing agents.

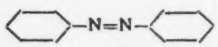
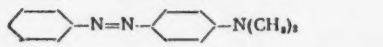
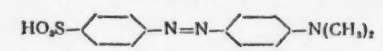
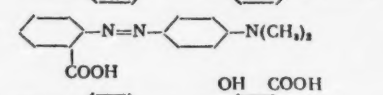
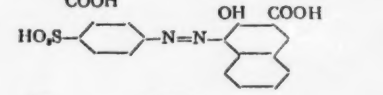
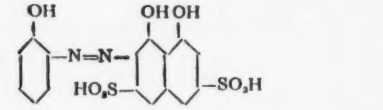
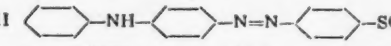
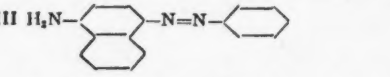
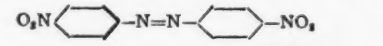
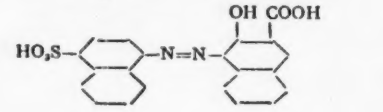
The molar absorption coefficients of the halochromic compounds of the azo dyes have high values, this ensures a high sensitivity for any analytical method based on their use, while the maximum of the absorption

* A report given at the Eighth Mendeleev Conference on General and Applied Chemistry.

band may be located in almost any part of the visible spectrum, depending on the dye chosen. This fact is also very important in choosing an azo dye as an analytical reagent.

TABLE 1

Some Properties of Mono Azo Dyes

Azo dye	λ_{max}, mμ	ε × 10⁻⁴	Solubility in H_2SO_4, %	Oxidizing agent for the azo dye
I 	430	2.1	>90	$KMnO_4$, $K_2Cr_2O_7$
II 	530	2.2	⩾1	$KMnO_4$, $K_2Cr_2O_7$, HVO_3, $Ce(SO_4)_2$
III 	500	4.8	⩾1	Ditto
IV 	500	4.2	⩾1	" "
V 	470	3.2	>60	" "
VI 	610	1.8	>60	" "
VII 	570	5.2	⩾1	" "
VIII 	530	4.0	⩾1	" "
IX 	430	2.0	>95	$KMnO_4$, $K_2Cr_2O_7$
	570	3.6	>80	Ditto

The presence in the azo dye of hydroxyl, carboxyl (carbonyl), and amino groups increases the solubility of the dye in H_2SO_4, while the groups $-NO_2$ and $-SO_3H$ lower it.

The appearance in the azo dye of electron donating groups leads to a shift in the maximum to the long wave region of the spectrum.

From published data and from the author's experiments it follows that, azo dyes under the conditions leading to the formation of halochromic compounds (e.g. with H_2SO_4 and $HClO_4$) behave as reducing agents for MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-}, VO_3^-, Ce^{IV}, Cl_2, Br_2, hypochlorites, chlorites, the corresponding bromine compounds, and as oxidizing agents, e.g., for Sn^{II}, Ti^{III} [10].

Experiments on the possibility of using azo dyes for analytical purposes were carried out by two variants: photometric and titrimetric.*

The Photometric Variant: Equimolar (molar concentrations $2 \cdot 10^{-4}$) solutions (60% by volume with respect to H_2SO_4) of the halochromic compounds of the azo dyes and the corresponding solutions of the inorganic oxidizing agents were poured together in varying volume relationships: the volumes of the mixtures were always made up to a constant value (10 ml) with 60% sulfuric acid.

* T. S. Zhigalkina participated in the experimental work.

In many cases the oxidation – reduction reactions proceeds rapidly; sometimes it lasts 30-60 minutes and even longer. The reaction rate depends on the nature of the dye, the value of the oxidation – reduction potential of the inorganic oxidizing agent, and on acid concentration; the nature of the acid also affects the oxidation – reduction potential of the oxidizing agent [13].

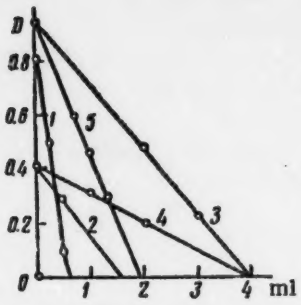


Fig. 2. The relation between the optical density of the halochromic compounds of the azo dye and the amount of oxidizing agent added [see Eqs. (1), (2), (3), (4), and (5)].

As soon as the optical density (D) of the mixture had become constant, it was measured on a photometer at λ_{max}. The experimental results are shown in Fig. 2.

It is clear from Fig. 2, that one volume (1 ml) of the azo dyes naphthyl red I, methyl orange III, V, and p-dimethylaminoazobenzene II, IV corresponds to the following volumes of solutions respectively: 0.66 ml $K_2Cr_2O_7$; 1.6 ml $KMnO_4$, 4.0 ml NH_4VO_3, 4.0 ml $Ce(SO_4)_2$, and 2.0 ml of Br_2 (bromine water).

A qualitative study of the reaction products showed that these could be nitrosubstituted diazo and azo components, mono and difunctional phenols, and their oxidation products – quinones; the composition of the products resulting from the oxidative break down of the azo dye depends on the nature of the oxidizing agent and the azo compound, and also on the time and reaction conditions.

Whether or not complete destruction occurs of the products resulting from the oxidative break down of the dye by the continued action of an inorganic oxidizing agent with a high oxidation potential, is of no interest for the problem under consideration.

A decisive influence on the rate, the extent, and the possibility of the oxidation process is apparently shown by the ratio of the oxidation – reduction potentials of the azo dye which forms the halochromic compound, and of the inorganic compound.

The following reactions can be adduced as examples.

Azobenzene is comparatively readily oxidized by permanganate ($E_0 = 1.52$ v, where E_0 is the normal oxidation – reduction potential), it is oxidized with slightly greater difficulty by dichromate ($E_0 = 1.36$ v), while it is not oxidized at all by vanadate ($E_0 = 1.08$ volt). It should be noted that the oxidation – reduction potentials of the oxidizing agents indicated are strongly dependent on the acid concentration (see [12]).

The mechanism of the oxidation – reduction reaction, obviously, differs for the various azo dyes and the various oxidizing agents. It should be noted, however, that the oxidation of azobenzene by dichromate, can, apparently, be represented in the following way:

$$\underset{\text{Halochromic compound}}{Ar{-}N(\cdot H_2SO_4)=N{-}Ar} \xrightarrow{O} \underset{\text{Diazo component}}{Ar{-}N(\cdot H_2SO_4)\equiv N} + \underset{\text{Azo component}}{HO{-}Ar} \xrightarrow{\text{coupling}} \underset{\text{Azoid form}}{Ar{-}N(\cdot H_2SO_4)=N{-}Ar{-}OH} \rightarrow$$

$$Ar{-}NH(\cdot H_2SO_4){-}N{=}Ar{=}O \xrightarrow{O} Ar{-}N(\cdot HSO_4)\equiv N + Ar(OH)_2;$$

Quinohydrazone form

$$Ar{-}N(\cdot HSO_4)\equiv N \xrightarrow{H_2O} Ar{-}OH + N_2 + H_2SO_4.$$

Further oxidation is possible

$$Ar(OH)_2 \xrightarrow{O} Ar(=O)_2 + H_2O.$$

It is known that during the oxidation of azobenzene by dichromate formation of p-hydroxyazobenzene occurs; the author has established that phenols (or quinone and phenol) are present.

Many facts are known [10] which indicate that the azo dye is in an azoid form in alkaline media and in a quinohydrazone form in acid media. In the scheme adduced above, we assumed that the p- and o-derivatives (with groups NR_2 and OH) of the azo dye participate in the reaction in the quinohydrazone form.

From an analytical point of view an important fact is that the decrease in optical density $D_0 - D$ of the halochromic compound is a linear function of the amount C of oxidizing agent added: $D_0 - D = K \cdot C$, where D_0 is the optical density of the original solution of the halochromic compound, D is the optical density of the solution of the halochromic compound after addition of a certain amount of oxidizing agent, K is the proportionality constant which determines the slope of the calibration curve and is dependent on the ratio of the stoichiometric coefficients in the equation of the reaction, and C is the amount of oxidizing agent added.

In this case the usual form of an ascending straight line is obtained within the coordinates $D_0 - D$ and C.

Nevertheless, any of the descending curves shown above (Fig. 2) can also be used as a calibration curve for the quantitative determination of the appropriate oxidizing agent. Using this relationship we have developed a method for the determination of vanadium in steels [1].

Titrimetric Variant. In those cases where the reaction proceeds rapidly, it is possible to titrate with the help of a solution of the halochromic compound of the azo dye, using it at the same time as the working material and as indicator.

In our work we used solutions of the dye and the oxidizing agent which had the same concentrations as in the photometric variant. The solvent was 60% (by volume) sulfuric acid.

Results for the titration of sulfuric acid solutions of the oxidizing agent by sulfuric acid solutions of the dye are given in Table 2.

TABLE 2

Titration of Certain Oxidizing Agents With an Azo Dye

Order of titration	Oxidizing agent, ml	Dye, ml	Ratio: oxidizing agent/dye	Notes
VO_3^- + Dye III	4.00	1.02	4 : 1	Titration was carried out to the appearance of the stable weak color of the dye (i.e., the color does not disappear)
	4.00	1.00		
	8.00	2.02		
Ce^{IV} + Dye II	4.00	1.02	4 : 1	Ditto
	4.00	1.00		
	8.00	2.02		
$Cr_2O_7^{2-}$ + Dye V	2.00	3.02	2 : 3	"
	2.00	3.02		
	4.00	4.04		
Methyl orange + MnO_4^-	4.00	2.50	8 : 5	Permanganate was added until the color of the dye disappeared
	8.02	5.00		
	7.98	5.00		

By using azo dyes in the form of their halochromic compounds with strong acids, it is possible, in principle, to determine small amounts of many oxidizing agents; two variants are possible: photometric and titrimetric. When the titrimetric variant is used, it is possible to carry out microtitration in which the concentration of the appropriate solutions are of the order of 10^{-4} M.

On the basis of the results given in Fig. 2 and Table 2, and also taking into account the scheme given above for the oxidation of azobenzene by dichromate, and the reaction products which were detected (qualitatively), it would seem possible to write the following approximate scheme for the oxidation – reduction reaction (the numbers given to the reactions correspond to the numbers on the straight lines in Fig. 2):

$$3H_2N-Ar-N=N-Ar + 2K_2Cr_2O_7 + 8H_2SO_4 =$$
$$3H_2N-Ar\begin{matrix}OH\\OH\end{matrix} + 3Ar-OH + 3N_2 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 5H_2O; \quad (1)$$

Phenol is readily detected in the reaction mixture. After neutralization of excess H_2SO_4, diazotization and subsequent coupling, a dye develops which is proof of the presence of an aromatic amine in the reaction mixture.

$$5Ar-N=N-Ar-N(CH_3)_2 + 8KMnO_4 + 12H_2SO_4 =$$
$$5Ar-OH + 5(CH_3)_2N-Ar-OH + 10HNO_2 + 8MnSO_4 + 4K_2SO_4 + 2H_2O. \quad (2)$$

The amount of permanganate added to the sulfuric acid solution of the dye, up to the point at which the dye is decolorized, corresponds to the stoichiometric coefficients (5 : 8) given above; however, after decolorization of the dye, the permanganate added continues to be decolorized rapidly up to the point where the amount of it added is equivalent to 10 g-mole of HNO_2; after this point the permanganate is decolorized very slowly (presumably, a more profound decomposition of the organic material occurs). After the reaction mixture has been allowed to stand, nitrophenol could be detected in it (qualitatively); this fact indicates that nitration of the diazo component may have occurred.

$$HO_3S-Ar-N=N-Ar-N(CH_3)_2 + 4HVO_3 + 4H_2SO_4 =$$
$$=HO_3S-Ar-OH + (CH_3)_2N-Ar\begin{matrix}OH\\OH\end{matrix} + N_2 + 4VOSO_4 + 5H_2O; \quad (3)$$

$$Ar-N=N-Ar-N(CH_3)_2 + 4Ce(SO_4)_2 + 3H_2O =$$
$$=Ar-OH + (CH_3)_2N-Ar\begin{matrix}OH\\OH\end{matrix} + N_2 + 2Ce_2(SO_4)_3 + 2H_2SO_4; \quad (4)$$

$$HO_3S-Ar-N=N-Ar-N(CH_3)_2 + 2Br_2 = HO_3S-Ar-NBr_2 + Br_2N-Ar-N(CH_3)_2 \quad (5)$$

The reaction Eq. (5) was written in accordance with the stoichiometric coefficients obtained experimentally, and by taking into account the data given in [9].

It must be emphasized that the question regarding the composition and structure of the reaction products obtained during the oxidation – reduction breakdown of azo dyes requires further study.

SUMMARY

The possibility has been demonstrated of the wide use of azo dyes as analytical oxidation – reduction reagents for the photometric and titrimetric determination of microgram amounts of a number of oxidizing agents.

A linear relationship has been established between the decrease in optical density of a solution of the halochromic compound of an azo dye and the amount of oxidizing agent added.

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MASKING OF CATIONS BY MEANS OF UNITHIOL DURING COMPLEXONOMETRIC TITRATIONS

Yu. V. Morachevskii and L. A. Vol'f

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Translated from Zhurnal Analiticheskoi Khimii, Vol. 15, No. 6, pp. 656-660, November-December, 1960
Original article submitted December 15, 1959

Unithiol (sodium 2,3-dimercaptopropanesulfonate) is a white, finely crystalline material, which is readily soluble in water and is fairly stable in solution. It is used medically as an antidote for poisoning by many heavy metals [1]. Dimercaptopropanol (the British product lewisite) possesses similar properties. The latter has been used as a masking agent in analytical practice [2]. In contrast to unithiol, however, dimercaptopropanol is insoluble in water and its stability is low in alcoholic solutions.

Unithiol is capable of forming stable complex compounds with a number of metals. The complex compounds of unithiol with certain metals – sodium metallodimercaptopropanesulfonates – are more stable in some instances than the corresponding complexonates. This permits the use of unithiol for masking during complexonometric determinations, particularly during titrations in ammoniacal media.

As our studies have shown, unithiol displaces ethylenediaminetetracetic acid (EDTA) from its compounds with elements of the zinc, germanium, and arsenic subgroups. At the same time, the presence of unithiol does not interfere with the determination of calcium and magnesium ions and also of strontium and barium.* Accordingly, during the complexonometric titration of these cations, all the metals of the subgroups indicated (with the exception of germanium, on which no experiments have been carried out) can be reliably masked with unithiol. Results for the determination of ions of the second analytical group in the presence of cations of some of the heavy metals are presented in Tables 1 and 2.

TABLE 1

Determination of Calcium and Magnesium in the Presence of Zinc, Lead, and Bismuth

Masking ions, mg			Ca, mg			Mg, mg		
Zn	Pb	Bi	taken	found	error	taken	found	error
33	—	—	19.68	19.64	—0.04	—	—	—
33	—	—	—	—	—	12.28	12.33	+0.05
—	86	—	19.68	19.64	—0.04	—	—	—
—	86	—	—	—	—	12.28	12.28	0
—	—	15	19.68	19.73	+0.05	—	—	—
—	—	15	—	—	—	12.28	12.26	—0.02

* Our work on this question has been sent for publication, and some of it has already been published in Zavodskaya Lab. 25, 1438 (1959), and Uch. Zap. Leningrad Gosud. Universiteta [in press].

In the same way it is possible to mask these cations during the complexonometric determination of lanthanum and,probably, other rare earths.

The complex compounds of unithiol with the elements of the zinc, germanium, and arsenic subgroups are not colored in an ammoniacal buffer medium. An exception is the yellow color of the complex of unithiol with bismuth and antimony. Accordingly, the permissible content of these cations in mixtures to be analyzed must be limited. At contents of these elements up to 20 mg in the solution being titrated, the color change of the indicator is clear enough at the end point.

TABLE 2

Determination of Strontium and Barium in the Presence of Zinc, Lead, and Bismuth

Masking ions, mg			Sr, mg			Ba, mg		
Zn	Pb	Bi	taken	found	error	taken	found	error
33	—	—	55.20	55.33	+0.13	—	—	—
33	—	—	—	—	—	74.49	74.04	—0.45
—	86	—	55.20	55.11	—0.09	—	—	—
—	86	—	—	—	—	74.49	74.49	0
—	—	15	55.20	55.11	—0.09	—	—	—
—	—	15	—	—	—	74.49	74.45	—0.04
—	—	6	5.687	5.700	+0.013	—	—	—
—	—	6	—	—	—	7.493	7.466	—0.027

Unithiol also forms complex compounds with silver, cobalt, copper, and iron. All these compounds are intensely colored in an ammoniacal medium and interfere with titration.

Unithiol interacts with manganese to form a brown-green colored compound. Manganese does not form a compound with sodium dimercaptopropane sulfonate when the unithiol is added to a solution which contains in addition, EDTA – Na, hydroxylamine, and triethanolamine. Accordingly, unithiol can also be used for the determination of manganese ions in mixtures with some other cations, in particular with zinc and lead (Table 3).

TABLE 3

Determination of Manganese in the Presence of Zinc or Lead

Mn, mg			Zn, mg			Pb, mg		
taken	found	error	taken	found	error	taken	found	error
16.73	16.69	—0.04	16.17	16.19	+0.02	—	—	—
16.73	16.74	+0.01	—	—	—	47.78	47.80	+0.02
8.828	8.844	+0.016	8.044	8.109	+0.065	—	—	—
8.828	8.818	—0.010	—	—	—	24.58	24.63	+0.05
1.653	1.655	+0.002	1.457	1.458	+0.001	—	—	—
1.653	1.651	—0.002	—	—	—	4.345	4.343	—0.002

Under such conditions, the determination is carried out as follows. The sum of the two cations is determined by direct titration with EDTA – Na, using eriochrome black as indicator, or by back titration with magnesium sulfate after adding EDTA – Na to the solution in a known excess. Unithiol is then added to the solution and the EDTA liberated titrated with magnesium sulfate.

Unithiol interacts with nickel to form a brown colored complex which is less stable than the corresponding complexonate. This permits separate determination of nickel in mixtures with cations which are masked by unithiol, e.g., with zinc or lead (Table 4). In this case, to the test solution, after addition of excess EDTA – Na solution and back titration with magnesium sulfate solution, unithiol solution is added, and the EDTA liberated again titrated with magnesium sulfate solution.

TABLE 4

Determination of Nickel in the Presence of Zinc or Lead

Ni, mg			Zn, mg			Pb, mg		
taken	found	error	taken	found	error	taken	found	error
14.60	14.56	—0.04	16.17	16.12	—0.05	—	—	—
14.60	14.62	+0.02	—	—	—	47.78	47.71	—0.07
7.124	7.106	—0.018	8.044	8.044	0	—	—	—
7.124	7.141	+0.017	—	—	—	24.58	24.67	+0.09
1.328	1.329	+0.001	1.457	1.455	—0.002	—	—	—
1.328	1.326	—0.002	—	—	—	4.345	4.354	+0.009

Sodium metallodimercaptopropanesulfonates are broken down by iodine and hydrogen peroxide. Accordingly, hydrogen peroxide can be used as an antireagent during masking with unithiol, so that it is possible to carry out successive complexonometric determinations of several cations in one aliquot (Table 5).

Unithiol can also be used as a masking reagent in combination with other masking agents, so that it is possible to increase the selectivity of complexonometric determinations.

TABLE 5

Successive Determinations of the Content of Alkaline Earth Elements in Zinc

Zn, mg			Ca, mg			Mg, mg		
taken	found	error	taken	found	error	taken	found	error
32.93	32.83	—0.10	20.28	20.34	+0.06	—	—	—
32.93	32.93	0	—	—	—	11.93	11.94	—0.04
15.307	15.323	+0.016	11.480	11.460	—0.020	—	—	—
15.307	15.356	+0.049	—	—	—	6.389	6.406	+0.017
2.575	2.582	+0.007	2.168	2.172	+0.004	—	—	—
2.575	2.566	—0.009	—	—	—	1.474	1.464	—0.010

It is important to note that the use of unithiol during masking of elements of the zinc subgroup enables one to do without potassium cyanide.

EXPERIMENTAL

1. Determination of Calcium and Magnesium Ions in the Presence of Zinc, Lead, and Bismuth Cations. To 10 ml of a 0.1 N solution of calcium chloride or magnesium chloride is added 10 ml of 0.1 N zinc or lead nitrate, or 10 ml of a bismuth nitrate solution in which the bismuth ion concentration is 1.5 g/liter. After adding to each of the samples 20 ml of a 2% aqueous solution of unithiol and 5-10 ml of an ammoniacal buffer solution with a pH of 10, the solution is diluted with distilled water to 100 ml, and some indicator – eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1:10) – added on a knife tip. The solution is finally titrated with 0.1 N EDTA-Na solution until the color of the solution changes from wine-red to blue.

2. Determination of Strontium and Barium Ions in the Presence of Zinc, Lead, and Bismuth Cations. To 10 ml of a 0.1 N solution of strontium nitrate or barium chloride is added 10 ml of a 0.1 N solution of zinc or lead nitrate. In this case to 10 ml of 0.1 N or 0.01 N solutions of these salts is added 10 ml of a solution of bismuth nitrate with a bismuth concentration of 1.5 g/liter or 0.6 g/liter. After adding to each of the samples 20 ml of a 2% aqueous solution of unithiol (in the case of 0.01 N solutions - 0.2% unithiol) and 5-10 ml of a 25% ammonia solution, the solution is diluted to 100 ml with distilled water. Next some indicator – cresolphthalein (a solid mixture of cresolphthalein, diamine green B, methyl red, and sodium chloride in the proportion 1:0.5:0.05:15) is added on a knife point, and the solution titrated with 0.1 N (in the case of 0.01 solutions – 0.01 N) EDTA – Na solution until the color of the solution changes from violet to green.

3. Determination of Manganese Content in the Presence of Zinc or Lead Ions. To a mixture of 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of manganese sulfate and 5 ml of 0.1 N, 0.05 N, or 0.01 N lead nitrate solution or zinc sulfate solution is added 0.1-1.0 g of hydroxylamine, 1-5 ml of a 30% solution of triethanolamine, and 5-10 ml of an ammoniacal buffer solution with a pH of 10; some indicator – eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1 :10) is added on a knife tip. After diluting the solution to 100 ml with distilled water the solution is titrated with 0.1 N, 0.05 N, or 0.01 N solutions respectively of EDTA – Na until the color changes from wine-red to blue. Ten ml of a 2%, 1%, or 0.2% solution, respectively, of unithiol is then added and the EDTA liberated titrated, depending on the concentration of the cations being determined, with a 0.1 N, 0.05 N, or 0.01 N solution of magnesium sulfate until the color of the indicator changes from blue to a dirty red.

4. Determination of Nickel in the Presence of Zinc or Lead Ions. To a mixture of 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of nickel nitrate and 5 ml of a 0.1 N, 0.05 N, or 0.01 N solution of zinc sulfate or lead nitrate, is added 5-10 ml of an ammoniacal buffer solution with a pH of 10, 20 ml of 0.1 N, 0.05 N, or 0.01 N solution of EDTA – Na, respectively, some indicator – eriochrome black (a solid mixture of eriochrome black and sodium chloride in the proportion of 1 :10) is then added on a knife tip. The solution is diluted to 100 ml with distilled water and titrated respectively with 0.1 N, 0.05 N, or 0.01 N magnesium sulfate until the color of the indicator changes from blue-violet to wine-red. Ten ml of a 2%, 1%, or 0.2% solution of unithiol, respectively, is added (depending on the concentration of the cations to be determined) and the EDTA liberated titrated with magnesium sulfate solution.

5. Successive Determinations of the Alkaline Earth Elements in Mixtures with Zinc Ions. To a mixture of 10 ml of a 0.1 N, 0.05 N, or 0.01 N solution of calcium sulfate or magnesium sulfate and 10 ml of a 0.1 N, 0.05 N, or 0.01 N solution of zinc sulfate is respectively added 20 ml of 2%, 1%, or 0.2% solution of unithiol, 5-10 ml of an ammoniacal buffer solution, pH 10, and eriochrome black (a solid mixture with sodium chloride in the proportion of 1 :10) added on a knife tip. After diluting the solution to 100 ml with distilled water, it is titrated with 0.1 N, 0.05 N, or 0.01 N EDTA – Na solution – depending on the concentration of the ions to be determined – until the color changes from wine-red to blue. To the solution is then added 1-5 ml of a 30% solution of hydrogen peroxide and the liberated zinc ions titrated with EDTA – Na solution until the blue color appears.

It has been established in this way that it is possible to use unithiol in analytical chemistry, and methods have been developed for masking heavy metal ions by means of unithiol during the complexonometric titration of calcium, magnesium, strontium, barium, manganese, nickel, and lanthanum.

SUMMARY

Unithiol (sodium 2,3-dimercaptopropanesulfonate) is capable of forming complex compounds – sodium metallodimercaptopropanesulfonates – with many heavy metal ions. The complexes of unithiol with the elements of the zinc, germanium, and arsenic subgroups are more stable than the corresponding ethylenediaminetetracetates. Unithiol hardly reacts at all with ions of elements belonging to the second analytical group and with lanthanum. Unithiol can, therefore, be used for masking during the complexonometric determination of these ions in the presence of zinc, cadmium, mercury, lead, tin, arsenic, antimony, and bismuth. Unithiol does not displace nickel, or manganese (in a medium of hydroxylamine and triethanolamine) from their ethylenediaminetetracetate complexes, so that it is possible to determine these ions in the presence of metals which are masked by unithiol. Unithiol is readily soluble in water and is fairly stable in solution.

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SOME AZOXY COMPOUNDS AS REAGENTS FOR CATIONS

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Azoxy compounds are quite similar in structure and in certain properties to azo compounds and azomethines, among which are found a number of important analytical reagents. In this connection we thought it would be interesting to study the possibility of using azoxy compounds in analytical chemistry, in particular for the photometric determination of cations.

A comparative study of the qualitative reactions of 2,2'-dihydroxyazoxybenzene (I), 2,2'-dihydroxyazobenzene (II), and salicylidene-2-aminophenol (III) with 60 cations by method A (see the experimental section) indicated that 2,2'-dihydroxyazoxybenzene had the highest sensitivity.

While I at a pH of 14 in the presence of small amounts of pyridine gives a highly selective color reaction with copper only, II and III under these conditions give color reactions with copper, cobalt, and nickel. At pH 4 this difference is even more clearly manifested: reagent I gives a color reaction with copper only, while reagent II gives a reaction with copper, zinc, aluminum, gallium, vanadium, indium, manganese, cobalt, nickel, and palladium, and reagent III gives a reaction with copper, vanadium, manganese, cobalt, and palladium.

Some of the characteristics of the reactions of reagents I-III with copper are given in Table 1.

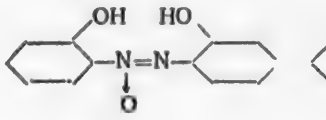
TABLE 1

Characteristics of Reagents I-III for Copper

Reagent	Maximum absorption, mμ		ε of reagent, ε of complex at λ	Visual sensitivity
	Reagents	Complex medium		
I	380	390	$2.5 \cdot 10^2$ $1.05 \cdot 10^4$ 430 mμ	0.25 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml
II	420	420	$2.3 \cdot 10^2$ $1.7 \cdot 10^4$ 520 mμ	0.1 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml
III	360	360	$8.7 \cdot 10^2$ $1.6 \cdot 10^4$ 420 mμ	0.15 μg Cu in 1 ml of the aqueous layer when the chloroform layer is 0.5 ml

As is evident, the increase in sensitivity observed on switching from the azo compounds tested and azomethine to the corresponding azoxy compound is accompanied by a drop in sensitivity. The fact indicated is, presumably, connected with the reduced complex formation tendency of the azoxy groups.

By including the azoxy group as an intermediate complex forming group in the system of a polydentate chelate former, we tried to find more effective reagents, in which the enhanced selective action of the azoxy group would be combined with an increase in complex formation as a result of the chelate effect. For this purpose, we synthesized and studied the following new compounds, containing in addition to o-hydroxyazoxy- or o-azo-azoxy groups, other chelate forming systems, they include: o-azoxyazo compounds from 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) and 2-naphthol (VI), H-acid (VII), R-salt (VIII), resorcinol (IX), 4,5-dimethylimidazole (X), the phenylhydrazone of benzoylformic acid,(XI) n-tolylhydroxylamine (XII), the α isomer of benzaldoxime (XIII),8-hydroxyquinoline-5-sulfonic acid (XIV), 2-naphthyliminodiacetic acid (XV), the azomethine from salicylaldehyde (XVI), and also o,o'-bisazoxy compounds from 2,2'-diaminoazoxybenzene (V), and 2-naphthol (XVII), p-cresol (XVIII), and H-acid (XIX).



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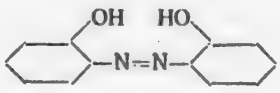

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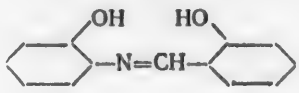

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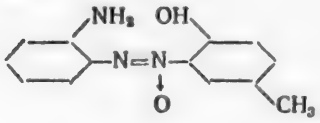

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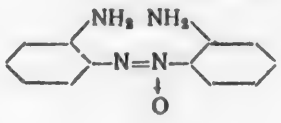

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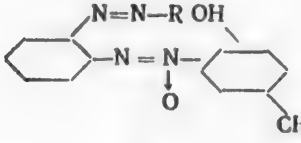

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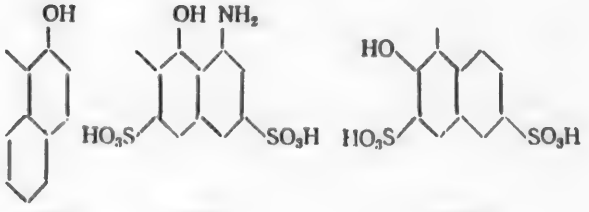
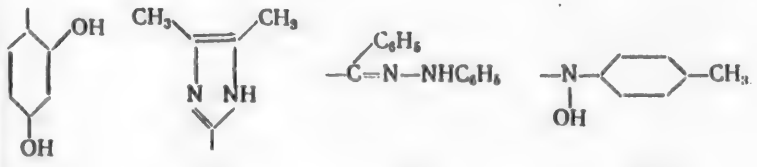
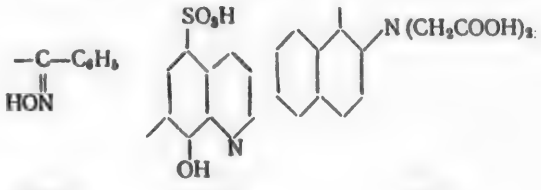


(VI) (VII) (VIII)



(IX) (X) (XI) (XII)



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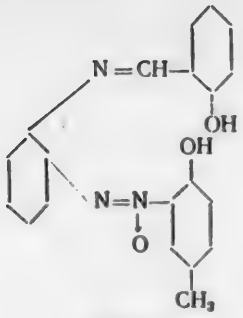

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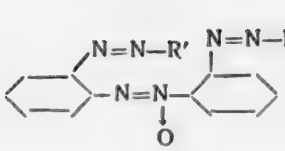

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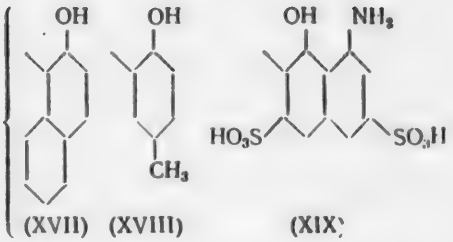

(XVII) (XVIII) (XIX)

Results of a study on the interactions of the synthesized compounds with 60 cations (Table 2) allow one to give the following general characteristics of the color reactions:

1. Reagents containing the o',o"-dihydroxy-o-azoazoxy group (reagents VI-IX), and also those similar in structure (X-XIII), as a rule, possess a fairly high selectivity. The most interesting of these reagents from the point of view of sensitivity and selectivity are reagents VI and VII.

TABLE 2

Characteristics of the Selectivity of the Reagents

Reagent	Ions which give color reactions (conditions !) (see experimental section)
VI	Cu. Co. Ca. Zn (pH 14)
VII	Cu, (pH 5—11); Mg, Zn, Bi, Fe^{II}, Co, Ni (pH 11); Pd (pH 1—5)
VIII	Cu, Ni, $Pt^{II, IV}$ (pH 1—11); Zn, Cd, La, Pd, Ir (pH 11); Sc, Co (pH 5—11)
IX	Cu, Ag, Co, Ni (pH 1—11); Zn (pH 5—11)
X	Cu, Ag, Zn, Mn (pH 5—11); Cd (pH 11); Co, Ni (pH 1—11); Pd (PH 1)
XI	Cu, Ca, Zn, Cd, Ga, Bi, Mo Mn, Co (pH 1—11)
XII	Cu, Co, Pd, (pH 1—11); Ca, Pb, (pH 11); Zn (pH 5—11); Ni (pH 1—5)
XIII	Cu, Co (pH 1=11); Zn, Cd (pH 5—11)
XIV	Cu, Ag, Ga (pH 11); Cd, Al, Sc, In, La, Fe^{II}, Ir (pH 5—11); Zr, Hf, Pb, Co (pH 1—11); Th (pH 1); Bi, Ni (pH 5); Pd, $Pt^{II, IV}$ (pH 1—5)
XV	Cu, Co, Pd, (pH 1—11); Ag, Zn, Cd, Mn (pH 11); V^{V}, Fe^{II} (pH 5); Cr^{III} (pH 1); Ni (pH 5—11)
XVI	Cu (pH 1—11); Zn (pH 11); V^{IV} (pH 1—5); Co (pH 5—11); Ni, Pd (pH 1)
XVII	Cu, Co (pH 5)
XVIII	Cu (pH 5—11)
XIX	Cu (pH 5—11); Co, Ni (pH 11); Pd (1—11)

2. Polydentate reagents containing, in addition to the o'-hydroxy-o-azoxyazo groups, other comparatively strong chelate forming systems – the partially isolated 8-hydroxyquinoline group* (reagent XIV) or the non-isolated group of iminodiacetic acid (reagent XV) – exhibit an appreciably lower selectivity in the color reactions with cations.

* According to the classification suggested by one of us [1], this reagent belongs to the type of bisreagents with a common donor group.

3. Reagent XVI which contains the o,o'-dihydroxy-o-azoxyazomethine group, gives color reactions with 6 out of the 60 cations. The pale-yellow color of the reagent solution changes to red in the presence of copper, to orange in the presence of zinc, while vanadium, nickel, cobalt, and palladium lead to a weak color change. However, the enhanced selectivity of this reagent is not accompanied by high sensitivity.

4. Reagents (XVII-XIX) containing the o,o'-bis-(o-hydroxyazo)-azoxy group is distinguished by a very high selectivity.

The most promising reagents were examined in greater detail.

Reagent VI in an alkaline medium, under the conditions of method A, gives a selective reaction with calcium. The color change is from a rose-orange to colorless. The sensitivity of the visual reaction is 0.5 μg of calcium in 0.5 ml of the aqueous volume, when the volume of the carbon tetrachloride is 1 ml. For λ_{max} of the reagent of 510 mμ, $\epsilon = 1.815 \cdot 10^4$. In addition to the reaction with calcium, the reagent only gives a color reaction with copper (a raspberry color), cobalt (red), while zinc gives a weak color change. Barium, strontium, magnesium, beryllium, etc. do not interfere with detection of calcium.

A comparison of the properties and the conditions under which reagent VI is used, with the analytical data relating to murexide [2] and "calcion IREA" [3] showed the advantages of the new reagent.

1) When murexide is used the color obtained is only stable for a few minutes, while the colors given by the new reagent are stable for several days;

2) calcium can be determined by means of the new reagent in the presence of considerably larger amounts of salts (10-20 times) than is possible when "calcion IREA" is used.

Reagent VII in an alkaline medium (pH 10-11) gives a selective reaction with zinc. The color of the reagent solution changes from red to blue-violet. The sensitivity of the visual reaction is 0.25 μg zinc in 5 ml of solution. λ_{max} for the reagent is 560 mμ, while λ_{max} for the complex is 580 mμ; $\epsilon_{reagent}$ is $8.3 \cdot 10^3$ at 620 mμ, while $\epsilon_{complex}$ is $2.4 \cdot 10^4$ at 620 mμ. In addition to zinc, under these conditions, intense color reactions are given by copper (blue-violet color), cobalt (green), nickel (green). Cadmium, mercury, lead, etc. do not interfere with the detection of zinc.

Reagent VII has the following advantages over "zincon" [4].

1) The sensitivity of reagent VII is twice that of "zincon";

2) Zinc can be determined with reagent VII in the presence of considerably greater amount of cadmium.

Reagent XIX gives a selective reaction with palladium at a pH of about 5. The color change is from lilac to a dirty-blue. The sensitivity of the visual reaction is 0.25 μg palladium in 5 ml of solution. λ_{max} of the reagent is 540 mμ, while λ_{max} for the complex is 360 mμ; $\epsilon_{reagent}$ is $1.57 \cdot 10^4$ at 540 mμ, while $\epsilon_{complex}$ is $5.5 \cdot 10^3$ at 540 mμ.

The remaining elements of the platinum group do not lead to a change in the color of the reagent solution.

In addition to palladium, under these conditions, intense color reactions are also given by copper (blue), cobalt (blue), and nickel (violet).

Thus the results obtained confirm our assumption re the possibility of making reagents with an enhanced selectivity by including a weakly complexing azoxy group in the system of a polydentate chelate forming agent.

EXPERIMENTAL

Synthesis of Reagents. 2,2'-dihydroxyazobenzene (I), 2,2'-dihydroxyazobenzene (II), and 2,2'-diamino-azoxybenzene (V) were synthesized according to published methods [5, 6, 7]. The m. p. of I was 156°. The published figure [5] was m. p. 154-155°. The m. p. of II was 171-172°, while the published m. p. [6] was 172-172.7°. The m. p. of V was 115-116°, while the published m. p. [7] was 115°. Salicylidene-2-amino-phenol (III) was presented by Lukin, its m.p. was 185.5-186.5° [8]. 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) was prepared according to [9]. The m. p. was 126°.

Found %: C 64.58, 64.29; H 5.62, 5.68; N 17.50, 17.36. $C_{13}H_{13}O_2N_3$. Calculated %: C 64.19; H 5.35; N 17.28.

General Observations on Synthesis

o', o"-Dihydroxy-o-azoazoxy compounds

The 2-amino-2'-hydroxy-5'-methylazoxybenzene in the filtrate obtained by the action of hydrazine on 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene [9] was diazotized and coupled with the azo component. Diazotization was carried out with excess sodium nitrite. Excess nitrous acid was destroyed with urea. 1.4 g-mole of the azo component was used per g-mole 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene. Coupling was carried out at 0-3°, the diazo solution was gradually added to the solution of the azo component. The dyes were isolated on the day following the coupling. The dyes were purified by reprecipitation or recrystallization from various solvents.

The theoretical yields indicated are given in all cases in terms of 2-phthaloylamino-2'-hydroxy-5'-methylazoxybenzene.

The methods used for purifying and isolating the dyes are given below.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2"-hydroxynaphthalene (VI) was synthesized according to [9].

2'-Hydroxy-5'-1'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-2")-1"-hydroxy-8"-aminonaphthalene-3",6"-disulfonic acid (VII) was dissolved in water and salted out with cooking salt. The yield was 23% of a dark-violet powder, readily soluble in water.

Found %: moisture content 7.6; NaCl 2.47; C 42.82, 42.79; N 10.44, 10.33; H 3.61, 3.54. $C_{23}H_{19}N_5O_9S_2$ assuming 7.6% moisture content 2.47 NaCl. Calculated %: C 43.3; H 3.81; N 10.9.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2"-hydroxynaphthalene-3",6"-disulfonic acid (VIII) was dissolved in NaOH and salted out with hydrochloric acid, it was washed with ice water and dried at 80-90°. Yield 20%.

Found %: C 50.17, 50.2; H 3.9, 4.0. $C_{23}H_{18}N_4O_9S_2$. Calculated %: C 49.64; H 3.23.

The powder which is dark-violet in color is readily soluble in water.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-2", 4"-dihydroxybenzene (IX) was purified by acidifying the alcoholic alkali solution. Yield. 14.6%.

Found %: C 62.09, 62.03; H 4.63, 4.84. $C_{19}H_{16}N_4O_4$. Calculated %: C 62.63; H 4.39.

The powder is dark-brown in color. The material chars at 210°.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-2")-4", 5"-dimethylimidazole (X) was purified by successive recrystallization from ethanol and dioxane, and dried at 70°. Yield 10.5%.

Found %: C 61.66, 61.87; H 5.56, 5.58. $C_{18}H_{18}N_6O_2$. Calculated %: C 61.71; H 5.14.

The powder is orange in color; m. p. 200-202°.

(2'-Hydroxy-5'-methylbenzene-[1'-azoxy-1]-benzene-2)-phenylformazylbenzene (XI) was dissolved in alcoholic alkali, it was then salted out with hydrochloric acid, filtered off, washed with water and dried in a vacuum desiccator over calcium chloride and phosphorus pentoxide. Yield 10%.

Found %: C 68.58, 68.4; H 5.11, 5.30. $C_{26}H_{22}N_6O_2$. Calculated %: C 69.33; H 4.88.

The powder is dark-bordeaux in color; m. p. 138°.

1"-(2-)2"-Hydroxy -5'-methyl-benzene-(1'-azoxy-1)-phenyl-(3"-)-p-tolyl-(3"-hydroxytriazene) (XII) was recrystallized from a mixture of ethanol and chloroform (2:1) and dried in a vacuum desiccator over calcium chloride. Yield 11.7%.

Found %: C 63.45, 63.43; H 5.32, 5.36. $C_{20}H_{19}N_5O_3$. Calculated %: C 66.66; H 5.01.

The powder is orange in color; m. p. 145°.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-N)-α-benzaldoxime (XIII) was recrystallized from a mixture of ethanol and chloroform (2:1) and dried in a vacuum desiccator over calcium chloride. Yield 10%.

Found %: C 64.13, 63.87; H 5.17, 4.98. $C_{20}H_{17}N_5O_3$. Calculated %: C 54.0; H 4.53.

The powder is brown in color. It chars at about 200°.

2'-Hydroxy-5-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-7")-8"-hydroxyquinoline-5"-sulfonic acid (XIV) was purified by acidifying its alcoholic alkaline solution. The powder is reddish-brown in color.

Found %: N 11.07 (the nitrogen content of the azo- and azoxygroups was determined vanadometrically). $C_{22}H_{17}N_5O_6S$. Calculated %: N 11.6.

2'-Hydroxy-5'-methylbenzene-(1'-azoxy-1)-benzene-(2-azo-1")-naphthalene 2"-iminodiacetic acid (XV) was purified by acidification of its alkaline solution. The powder is brown in color; m. p. 115-117°.

Found %: C 60.3, 60.6; H 5.07, 5.3. $C_{27}H_{23}N_5O_6 \cdot 1.5\ H_2O$. Calculated %: C 60.0; H 4.8.

1-Azoxyazomethine compound (XVI) obtained from 2-amino-2'-hydroxy-5'-methylazoxybenzene (IV) and salicaldehyde. To 0.002 g-mole of IV in ethanol was added 0.0025 g-mole of salicaldehyde, the mixture was heated for 30 minutes at 60-70°; the precipitate was then filtered off, washed with ethanol, recrystallized from 40 ml of a mixture of petroleum ether and chloroform (3:1), and dried in a vacuum desiccator over calcium chloride. The powder is yellow in color; m. p. 180°.

Found %: C 67.7, 67.95; H 5.51, 5.38; N 11.41, 11.37. $C_{20}H_{17}N_3O_3 \cdot 0.5\ H_2O$. Calculated %: C 67.4; H 5.06; N 11.8.

o,o'-Bisazoazoxy compounds obtained from 2,2'-diaminoazoxybenzene and 2-naphthol (XVII), p-cresol (XVIII), and H-acid (XIX). 2,2'-diaminohydroxybenzene was diazotized and coupled with 2-naphthol (2M), p-cresol (2M), and H-acid (2M). Coupling was carried out in a soda-alkaline medium. XVII was purified by successive reprecipitation of the acid from alcoholic alkali, and by petroleum ether from chloroform. The powder has a cherry red color; m. p. 238°.

Found %: C 71.55, 71.69; H 4.97, 5.0. $C_{32}H_{22}N_6O_3$. Calculated %: C 71.50; H 4.13.

Dye XVIII was dissolved in benzene and precipitated by petroleum ether. The powder is brown in color; m. p. 135°.

Found %: N 18.89, 18.60. $C_{26}H_{22}N_6O_3$. Calculated %: N 18.02.

Dye XIX was dissolved in water and salted out with cooking salt. The material was not obtained in a chemically pure state.

Test Methods

Method A (Extraction with nonaqueous solvents). Reagents (I-VI, IX-XIII, XV, XVI-XVIII) which are insoluble in water were tested in the form of their 0.001 M chloroform solutions. Into four microtubes were introduced successively 0.5 ml of the extractant, 0.15 ml of reagent solution, and 0.06 ml of 2 M NaOH, while, in addition, to the first three tubes was added 0.06 ml of the corresponding standard solutions of the inorganic salts (100 μg of the cation). To the fourth tube was added 0.06 ml of distilled water (control test); the tubes were then all shaken and any change in the color of the organic layer or the appearance of a precipitate noted. Shaking was carried out for about 1 minute. Subsequently, the solutions were titrated in succession with acid reagents (1 M CH_3COOH, glacial acetic acid, HNO_3 1:2, and H_2SO_4 1:3). Each color change in the organic layer was observed and a note was made at which pH values of the solutions this effect was observed. Chloroform was used as extractant. Carbon tetrachloride was used for extracting reagent VI. In parallel, experiments were carried out in which pyridine was also introduced (after addition of the reagent) at the rate of about 0.03 ml per 0.5 ml of organic solvent. During a study of the sensitivity of the reaction, the pH of the solutions was kept constant by means of buffer solutions.

Method B (Experiments in aqueous solutions). The reagents which are soluble in water VII, VIII, XIV, and XIX were tested in the form of their 0.01-0.001% aqueous solutions.

Into 12 test tubes were introduced 1 ml lots of reagent solution, this was followed by adding: to the first and second test tubes, 0.06 ml of a 10% solution of acetic acid and 0.45 ml of 15% sodium acetate solution (pH about 5.8); to the third and fourth test tubes, 0.03 ml of hydrochloric acid and 0.3 ml of a 20% solution of urotropine (pH about 6); to the fifth and sixth test tubes, 0.06 ml of a 10% solution of Na_2CO_3 (pH about 10); to the seventh and eighth, 0.06 ml of a 10% solution of NaOH (pH about 13); to the ninth and tenth test tubes, 0.09 ml of a 10% solution of ammonium chloride, 0.15 ml of 1% ammonia, and 0.18 ml of 25% solution of ammonia (pH about 9); to the eleventh, 0.09 ml of HNO_3 (1 : 3) (pH 1), after which to all the test tubes with an odd number was added 0.06 ml of the corresponding standard solutions of the inorganic salts (100 μg of the cation), while to all even numbered test tubes was added 0.06 ml of distilled water (control test). The test tubes were shaken and any changes in color of the solution noted. Shaking was carried out for 1 minute.

The Change in the Optical Density of the Solutions.* Concentration of reagent I, $4.35 \cdot 10^{-5}$ M, copper concentration $1.5 \cdot 10^{-5}$ g-atom/liter; concentration of reagent II, $4.7 \cdot 10^{-5}$ M, copper concentration $6.45 \cdot 10^{-6}$ g-atom/liter; concentration of reagent III, $4.8 \cdot 10^{-5}$ M, copper concentration $9 \cdot 10^{-6}$ g-atom/liter; concentration of reagent VI, $2.5 \cdot 10^{-5}$ M, concentration of reagent VII, $7 \cdot 10^{-5}$ M; zinc was taken in a 32-fold molar excess with respect to the reagent; concentration of reagent XIX, $1.1 \cdot 10^{-5}$ M; palladium was taken in a 32-fold molar excess with respect to the reagent. The pH of the solutions was kept constant by means of a buffer with a pH of 10 for reagents I-III, with a pH of 14 for reagent VI, and with a pH of 5 for reagent XIX. Reagents I, II, III, and VI which are insoluble in water were dissolved in chloroform (reagents I-III) or carbon tetrachloride (reagent VI), and mixed, in the case of reagents I-III, VII with a buffer which had a pH of 10.6, in the case of reagent VI with a buffer with a pH of 14, and in the case of XIX with a buffer with a pH of 5, and with an aqueous solution of the salt of the cation. The ratio of the aqueous and nonaqueous phases was 1 : 20 by volume. In the case of reagents I-III, 0.05 ml of pyridine was added for 20 ml of chloroform. The mixture was shaken for 5-10 minutes; the nonaqueous layer was filtered off and the optical density measured on a SF-4 spectrophotometer, the thickness of the layer in the cuvette being 1.0 cm; the optical density was measured relative to chloroform for reagents I-III, to carbon tetrachloride for reagent VI, and to water for reagents VII and XIX.

The optical density of complexes for reagents I-III was calculated on the basis of the cation concentration, and for reagents VII and XIX on the basis of the molar concentration of the reagent. The optical density for all the reagents was calculated with respect to the amount of reagent added initially.

SUMMARY

The enhanced selectivity of 2,2'-dihydroxyazoxybenzene as compared with that of the analogous azo- and azomethine compounds has been established in reactions with cations.

The inclusion of an azoxy group in the system of a polydentate chelate forming agent leads to the formation of sensitive reagents with enhanced selectivity.

Among o',o"-dihydroxyazoxyazo compounds and o,o'-bis-(o-hydroxyazo)-azoxy compounds, reagents have been found which are of interest for the photometric determination of calcium, zinc, and palladium.

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THE REDUCING PROPERTIES OF ETHYLENEDIAMINETETRACETIC ACID

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Published data of a qualitative character [1-5] testify to the fact that under certain conditions, Ce^{IV}, Mn^{VII}, V^{V}, $S_2O_8^{2-}$, etc. oxidize ethylenediaminetetracetic acid (EDTA). Establishment of the quantitative relationships which hold during the oxidation of EDTA is of definite interest for solving a number of analytical problems. Our work was therefore directed at a detailed study of the reducing properties of EDTA and its salts.

The following materials were used: 1) sodium ethylenediaminetetracetate (EDTA – Na) (molecular wt. 372.2) which was purified by precipitation with methanol from an aqueous solution [6], and EDTA which was obtained from its sodium salt [7].

2) Solutions of the oxidizing agents: 0.043 M solution of ceric sulfate; 0.080 M ammonium vanadate; and 0.100 M potassium permanganate.

3) 0.027 M and 0.05 M solutions of EDTA – Na.

Experiments showed that the permanganate ion in a 1-2 N solution of sulfuric acid can be quantitatively titrated with EDTA-Na solution (and vice versa) in the cold. The titration end point was established visually from the disappearance of the permanganate color. The titration results are given in Table 1.

TABLE 1

Titration of 0.100 N $KMnO_4$ Solution with 0.027 M EDTA-Na

Amount of $KMnO_4$, g-eq $\times 10^{-3}$	Amt. of EDTA-Na used, g-mole $\times 10^{-3}$	Ratio of EDTA-Na (g-mole) to Mn^{VII} (g-eq.)
0.100	0.0124	1 : 8.05
0.100	0.0127	1 : 7.87
0.100	0.0124	1 : 8.05
0.200	0.0248	1 : 8.05

Complete decolorization is observed at a ratio of one mole of EDTA-Na to eight gram equivalents of the oxidizing agent.

Results for the titration of 0.043 M ceric sulfate solution with 0.050 M EDTA-Na at a pH of 1-1.5 in the cold, and on warming, are given in Table 2 (the titration end point was again determined visually by the disappearance of the color of quadrivalent cerium). Quadrivalent cerium in an acid medium (pH 1-1.5) reacts with EDTA-Na in the cold in the proportion of 1 : 4, while on heating, it reacts in the proportion of 1 : 8.

Quinquevalent vanadium and sexivalent chromium, as experiments showed, are reduced in an acid medium (1 N H_2SO_4) only on heating, and in the presence of excess EDTA-Na.

TABLE 2

Titration of $Ce(SO_4)_2$ with EDTA-Na (0.215 g-eq of Ce^{IV} taken)

Experimental conditions	EDTA-Na used, g-mole × 10^{-3}	Ratio of EDTA-Na (g-mole) to Ce^{IV} (g-eq.)
In the cold	0.0540	1 : 4.0
In the cold	0.0545	1 : 3.95
On heating	0.0270	1 : 8.0
On heating	0.0265	1 : 8.1

During the oxidation of EDTA by septivalent manganese, quinquevalent vanadium, etc., carbon dioxide is liberated. Results on the quantitative determination of the carbon dioxide formed during the oxidation of EDTA-Na (by absorbing the CO_2 with askarite) are given in Table 3. With increasing ratio of oxidizing agent (Ce^{IV} or Mn^{VII}) to EDTA, the number of moles of carbon dioxide liberated per mole of EDTA-Na increases (figure).

TABLE 3

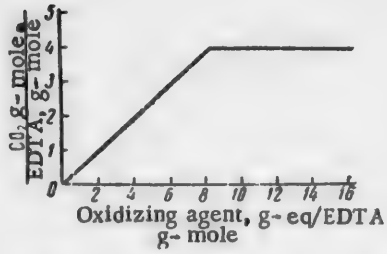
Amount of CO_2 Formed During the Oxidation of EDTA by Solutions of Ce^{IV}, Mn^{VII}, and V^{V} (on heating in a medium of 1 N H_2SO_4)

Oxidizing agent	Amt. of oxidizing agent, g-eq. × 10^{-3}	EDTA-Na added, g-mole × × 10^{-3}	Ratio of EDTA-Na (g-mole) to oxidizing agent (g-eq)	CO_2 liberated, g-mole × × 10^{-3}	Ratio of CO_2 (g-mole) to oxidizing agent (g-eq)	Ratio of CO_2 (g-mole) to EDTA-Na (g-mole)
Ce^{IV}	0.210	0.430	2 : 1	0.100	1 : 2	0.23 : 1
	0.210	0.210	1 : 1	0.097	1 : 2	0.46 : 1
	0.420	0.460*	1 : 1	0.200	1 : 2	0.43 : 1
	0.210	0.105	1 : 2	0.100	1 : 2	1 : 1
	0.210	0.053	1 : 4	0.095	1 : 2	1.8 : 1
	0.210	0.042	1 : 5	0.100	1 : 2	2.4 : 1
	0.210	0.035	1 : 6	0.097	1 : 2	2.8 : 1
	0.210	0.027	1 : 8	0.100	1 : 2	3.7 : 1
	0.420	0.053	1 : 8	0.200	1 : 2	3.8 : 1
	0.210	0.021	1 : 10	0.084	1 : 2.5	4 : 1
	0.210	0.014	1 : 15	0.048	1 : 4.4	3.4 : 1
V^{V}	0.400	1.60	4:1	0.200	1 : 2	—
	0.800	2.00	2.5 : 1	0.400	1 : 2	—
	0.800	2.00*	2.5 : 1	0.400	1 : 2	—
	0.400	0.80	2 : 1	0.200	1 : 2	—
	0.800	1.60	2 : 1	0.400	1 : 2	—
	0.800	0.80	1 : 1	0.300	1 : 2.7	—
	0.800	0.40	1 : 2	0.130	1 : 6	
Mn^{VII}	0.100	0.020	1 : 5	0.046	1 : 2.1	2.3 : 1
	0.100	0.012*	1 : 8.3	0.046	1 : 2.1	3.8 : 1
	0.100	0.012	1 : 8.3	0.048	1 : 2.0	4 : 1
	0.200	0.024	1 : 8.3	0.095	1 : 2.1	4 : 1
	0.100	0.010	1 : 10	0.043	1 : 2.3	4.3 : 1

* An accurately weighed aliquot of EDTA was taken.

During the oxidation of EDTA there is observed on the curves (figure) a break at a ratio of oxidizing agent g-eq. to EDTA equal to 8 : 1, corresponding to the liberation of four moles of carbon dioxide to one mole of EDTA; on increasing the amount of oxidizing agent further, this ratio remains constant and equal to

four. Accordingly, in an acid medium, the molecule of ethylenediaminetetracetic acid, under the influence of the oxidizing agent, breaks down to yield four molecules of carbon dioxide; during this process, it is obviously the carboxyl groups which break down.



Liberation of CO_2 during oxidation of EDTA by $Ce(SO_4)_2$ and $KMnO_4$ solutions.

EDTA is used in several analytical methods in combination with hydrogen peroxide, but the possibility of the oxidation of the EDTA has not been taken into account. According to our observations, EDTA is oxidized by excess 30% hydrogen peroxide in both acid and alkaline media. On heating to the boil this reaction proceeds quantitatively in a few minutes; in the cold only about 20% of the EDTA is oxidized in 18-20 hours (this was established by titrating the residual EDTA with a magnesium salt solution). We were unable to isolate and identify any other oxidation products of EDTA, apart from CO_2. It should be pointed out that Czech workers [8] during a polarographic study of the products obtained during the oxidation of EDTA by lead peroxide, demonstrated that formaldehyde is formed. In addition, these authors suggest the formation of products formed by the condensation of formaldehyde with amines, which are also obtained during the oxidation of EDTA.

SUMMARY

It has been found that ethylenediaminetetracetic acid (EDTA) interacts with septivalent manganese (in 1-2 N H_2SO_4) in the proportion of one mole of EDTA to eight gram equivalents of the oxidizing agent; in the case of quadrivalent cerium the relationship indicated is only observed on heating.

Quinquevalent vanadium and sexivalent chromium are reduced in an acid medium, only on heating and in the presence of excess EDTA.

Excess hydrogen peroxide, in both acid and alkali media, oxidizes EDTA; the reaction is quantitative and rapid only when the solution is boiled.

In acid media the EDTA molecule breaks down under the influence of oxidizing agents to liberate four molecules of carbon dioxide.

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A NEW REDOX INDICATOR FOR TITRATION IN ALKALINE MEDIA

THE FERRICYANIDE METHOD FOR THE DETERMINATION OF VANADIUM

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Oxidimetry in alkaline media has been developed to a comparatively small extent. It is only in recent years that papers have started to appear which are devoted to the determination of oxidizing or reducing agents in alkaline media [1-9]. In most cases, the methods described in these papers have a potentiometric finish. Various diphenylamine derivatives [10] have been tested as redox indicators under the conditions indicated; diphenylaminosulfonic acid in the oxidized form has proved to be best indicator. When it is borne in mind that this compound only has a low sensitivity, that its oxidation products exhibit maximum absorption on the short wave side of the visible spectrum, and that is not very easy to prepare the "polyoxidized" form of this indicator, it is quite obvious that it is necessary to make a further search for indicators which are suitable for oxidation – reduction titrations in alkaline media.

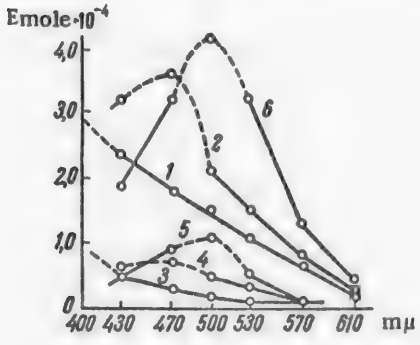


Fig. 1. Light absorption curves for $0.68 \cdot 10^{-4}$ M solutions of the reagents (oxidizing agent – potassium ferricyanide). 1) Diphenylbenzidene-o,o'-dicarboxylic acid; 2) diphenyltolidene-o,o'-dicarboxylic acid; 3) phenylanthranilic acid; 4) o-tolylanthranilic acid; 5) o-anisidene-anthranilic acid; 6) diphenyldianisidine-o,o'-dicarboxylic acid.

It was shown recently in our laboratories that certain diphenylbenzidene derivatives possess high sensitivity toward oxidizing agents at high pH values [11], although their oxidation products too exhibit maximum light absorption in the short-wave region of the spectrum. But, e.g., diphenyldianisidine-o,o'-dicarboxylic acid, which we shall henceforth refer to as "redoxal", and which we were the first to synthesize, possesses a high sensitivity to oxidizing agents in alkaline media and has a soluble oxidized form bright-red in color (Fig. 1). The indicator exhibits the maximum sensitivity for the ferricyanide ion in an alkaline medium, as compared with the other materials studied (Table 1).

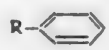
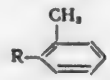
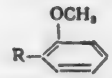
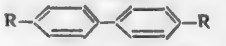
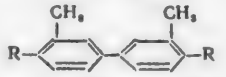
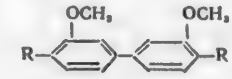
The oxidation-reduction potential of redoxal in 1 M potassium hydroxide proved to be equal to 0.304 v with respect to the normal hydrogen electrode. The oxidized form of the indicator, as indicated already, is bright red in color, while the reduced form is colorless; the color change is reversible.

During the interaction of the reagent studied with potassium ferricyanide in an alkaline medium, the color appears instantaneously and reaches a maximum in 2.5 minutes. This latter fact does not impose any limitations on the use of the indicator, this is demonstrated by the curve shown in Fig. 2 which characterizes the change in optical density of a solution of the indicator with time. In the

same diagram are also given curves which show that excess oxidizing agent has hardly any effect on the color intensity of the oxidized form of the indicator.

TABLE 1

Sensitivity of Some Diphenylamine and Diphenylbenzidene Derivatives to the Ferricyanide Ion In An Alkaline Medium (Determined by a Spot Test)

Reagent	Formula	Color of the reaction product	Lim. of ident. μg	Limiting dilution
1. Phenylanthranilic acid		Brown-yellow	230	1 : 4300
2. o-Tolylanthranilic acid		Red-brown	23	1 : 43 000
3. o-Methoxyphenyl-anthranilic acid		Red	23	1 : 43 000
4. Diphenylbenzidene-o,o'-dicarboxylic acid		Brown-yellow	2.3	1 : 430 000
5. Diphenyltolidene-o,o'-dicarboxylic acid		Red-brown	0.5	1 : 2 000 000
6. Diphenyldianisidine-o,o'-dicarboxylic acid		Red	0.4	1 : 2 500 000

The color formed is stable on diluting the solution (Table 2). Figure 3 shows that changes in alkalinity over a wide range do not affect the rate at which the maximum color develops.

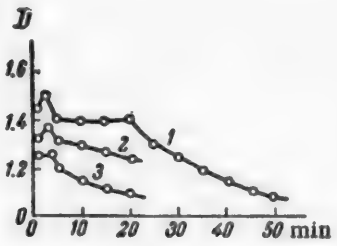


Fig. 2. Stability of the color of redoxal in the oxidized form with time. 1) 0.33 ml of 10^{-3} M solution of redoxal, 0.66 ml of 10^{-3} M potassium ferricyanide, and 4 ml of 0.1 N sodium hydroxide; 2) ditto, but with 1.32 ml of ferricyanide; 3) ditto but with 2.00 ml of ferricyanide.

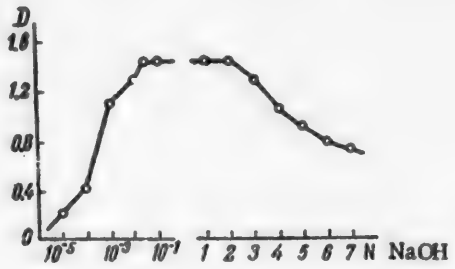


Fig. 3. Effect of sodium hydroxide concentration on the color intensity of the oxidized form of redoxal (0.3 ml of 10^{-3} M redoxal solution, 0.66 ml 10^{-3} M potassium ferricyanide, and 4 ml of sodium hydroxide solution of varying concentration).

We have studied the possibility of using redoxal as a redox indicator for the titration of ferricyanide with quadrivalent vanadium salts. 0.05 N solutions of vanadyl tartrate and vanadyl sulfate were used as reducing agents; vanadyl sulfate was prepared according to the method of Willard and Manalo [10]. The concentration of the vanadyl sulfate solution was determined by means of permanganate [13], while that of the ferricyanide was determined iodometrically [12].

The indicator was prepared by dissolving 0.0240 g of diphenyldianisidine-o,o'-dicarboxylic acid and 0.0240 g of sodium carbonate in 50 ml of water.

TABLE 2

The Stability of the Color of Oxidized Redoxal on Diluting with 0.1 N Alkali ($C_{initial} = 5 \cdot 10^{-5}$ M; l = 0.5 cm)

Solution	Optical density
Original	1.41
Diluted 1:1	0.70
Diluted 1:4	0.35
Diluted 1:8	0.18

Titration was carried out as follows: to 5 ml of $5 \cdot 10^{-2}$ or $5 \cdot 10^{-3}$ N potassium ferricyanide solution was added 20 ml of water and the corresponding amount of 10 N NaOH; Saratov natural gas* was passed through the solution for 10 minutes to remove dissolved oxygen; after addition of three drops of the indicator solution and one drop of cupric sulfate,** titration was carried out with an equimolar solution of vanadyl sulfate or vanadyl tartrate, until the red color of the solution being titrated changed instantaneously to a yellow-green color or the solution became colorless.

The experimental results obtained are summarized in Table 3.

TABLE 3

Effect of Alkalinity and Dilution on the Accuracy of Titrating Potassium Ferricyanide Solution with Solutions of Vanadyl Sulfate and Vanadyl Tartrate, Using Redoxal as Indicator

Conc. of titrated sol., g-mole/liter		$5 \cdot 10^{-3}$					$5 \cdot 10^{-3}$	
Expt. No.		1	2	3	4	6	1	2
Amount of 10 N NaOH added to the solution being titrated, ml		0.5	1.0	2.0	5.0	10.0	2.5	5.0
Solution used, ml	Vanadyl sulfate	5.10	5.00	5.00	5.00	4.96	4.98	4.96
	Vanadyl tartrate	4.90	5.00	5.00	5.00	4.96	4.98	4.96

Back titration of the reducing agent with vanadyl sulfate as oxidizing agent is impossible, since, in an alkaline medium, it changes into the hydroxide. Vanadyl tartrate under these conditions, although it does not give a precipitate, gives low results during titration, as is evident from Table 4, in which are given results obtained under the following conditions: to 20 ml of water was added a definite amount of 10 N NaOH and natural gas passed through the solution for 10 minutes, 5 ml of $5 \cdot 10^{-2}$ N vanadyl tartrate was then added, followed by 2-3 drops of indicator solution and one drop of cupric sulfate; the solution was finally titrated with $5 \cdot 10^{-2}$ N potassium ferricyanide. The color change is sharp, from green to red.

Quadrivalent vanadium and tartaric acid in an acid medium forms [14] a complex $[VO(HC_4H_4O_6)]^+$, while at pH 6 the complex $[VO(C_4H_4O_6)_2]^{2-}$ is formed; the latter is stable in alkaline media. In this connection, we have made an attempt to determine vanadium in the form of vanadyl tartrate by adding sodium potassium tartrate to a solution of ammonium vanadate*** on heating, and rapidly titrating the hot solution with potassium ferricyanide after making the solution alkaline.

* Replacement of the natural gas by nitrogen has no effect on the experimental accuracy; oxidation of sulfur compounds, which may be present in the gas, by the potassium ferricyanide, occurs, as is well-known, under fairly rigorous conditions [9].

** Cupric ions increase the rate at which the ferricyanide reacts with quadrivalent vanadium salts.

*** Tartaric and citric acids, and their salts, convert VO_3^- to VO^{2+} [15].

We found that determination of vanadium can indeed be carried out in this way, it is even possible to titrate 10^{-3} N solutions; there is no need to pass an inert gas through the solution in this case (Table 5).

TABLE 4

The Possibility of Titrating Vanadyl Tartrate with $5 \cdot 10^{-2}$ N Potassium Ferricyanide Solution in the Presence of Redoxal

Expt. No.	1	2	3	4
Amt. of 10 *N* NaOH, added, ml	0.5	1.0	2.0	5.0
Amount of $5 \cdot 10^{-2}$ *N* ferricyanide solution used, ml	4.78	4.90	4.90	4.90

Six times its amount of chromium, twice its amount of manganese, twice its amount of molybdenum, and 12 times its amount of tungsten do not interfere with the determination of vanadium. Nickel and trivalent iron can be present in large amounts; cobalt and divalent iron (as its complex with tartaric acid) are titrated in the same way with potassium ferricyanide under the experimental conditions used.

The method suggested for the determination of vanadium is applicable to the analysis of iron based alloys (steel, ferrovanadium). The method is particularly suitable for the analysis of high silicon rocks, containing vanadium, since, by using this method, it is possible to avoid the lengthy process of removing silicic acid.

TABLE 5

Effect of Alkalinity on the Accuracy of Titration with Potassium Ferricyanide of Vanadyl Tartrate Obtained by Reduction of Ammonium Vanadate with Tartaric Acid (11.40 mg V taken)

NaOH concentration, N	V found, mg
1.2	11.11
2.2	11.37
3.0	11.37
3.6	11.37
4.2	11.37
4.5	11.37

TABLE 6

Determination of Vanadium in Rocks

Sample No.	Vanadium found, %	
	colorimetrically as a heteropolyacid [16]	by the suggested method
1	0.73	0.76
2	0.47	0.48
3	1.75	1.80
4	1.19	1.22

Vanadium is determined in rocks as follows: one g of finely ground sample is fused with a mixture of 4 g of sodium carbonate and 2 g of potassium carbonate. The melt is leached with hot water. The precipitate of sesquioxides is filtered off. The filtrate is placed in a 100 ml standard flask. An aliquot of the solution (10-20 ml) is acidified with sulfuric acid (using congo red paper), 10 ml of a saturated solution of sodium potassium tartrate is added and the whole heated to the boiling point, and then boiled for 1-2 minutes. The yellow color of the test solution, which is determined by the presence of the compound of quinquevalent vanadium with tartrate, disappears, and the solution acquires a blue color when large amounts of vanadium are present. To the hot solution is added 10 ml of 40% sodium hydroxide, three drops of indicator solution, one drop of a 1% cupric sulfate solution and the final solution titrated with .01N potassium ferricyanide until a red color appears. The potassium ferricyanide solution is standardized against ammonium vanadate under identical conditions.

The method was tried out on four samples of rock (Table 6).

For the analysis of steel, 0.3000 g is dissolved in 20 ml of hydrochloric acid 1:1. When the sample has dissolved completely the solution is heated to the boil, 5 ml of concentrated nitric acid is added, and the solution boiled to remove nitrogen oxides. The tungstic acid precipitate formed is filtered off and the filtrate collected in a 100 ml standard flask. The sesquioxides are precipitated in the standard flask with 40% sodium

hydroxide, a small excess of the latter being taken (1-2 ml). The contents of the flask are made up to volume with water, the whole carefully mixed, and then filtered into a dry flask. 10-20 ml of the filtrate is taken for titration, and the procedure given for the analysis of rocks then followed. When the vanadium content of the steel is less than 1%, 50 ml of the filtrate is taken for titration. For the analysis of ferrovanadium the amount of sample taken is reduced to 0.1000 g.

The method gives good results for steels with a high tungsten content; steels which contain molybdenum cannot, however, be analyzed by this method.

An idea of the accuracy of the method can be gained from the results given in Table 7.

TABLE 7

Determination of Vanadium in Iron Based Alloys

Sample	Specified vanadium content, %	Vanadium found, %
Ferrovanadium, Standard Sample 77	38.42	38.88; 38.79; 38.46
Steel, Standard Sample 87	2.26	2.20; 2.22
" " " 26 b	1.17	1.24; 1.22
" " " 122	1.85	1.81; 1.80
Steel, vanadium-nickel	0.26	0.24; 0.26
Steel, chrome-vanadium-tungsten	2.23	2.38; 2.30

Synthesis of Diphenyldianisidine-o,o'-dicarboxylic Acid. Twenty ml of isoamyl alcohol, 2.5 g of o-chlorobenzoic acid, 2 g of o-dianisidine, 2.7 g of potassium carbonate, and 0.1 g of powdered copper metal are boiled for two hours under reflux. The isoamyl alcohol is removed by steam distillation, and the acid precipitated from the solution of its potassium salt with hydrochloric acid solution 1:1. The material is purified by reprecipitation, and then by dissolving in ethanol on heating, and precipitating with water. The diphenyldianisidine-o,o'-dicarboxylic acid purified in this way is a light-green powder with an indefinite m. p. of about 300°. The molecular weight as determined by Rast's method (in benzoic acid) proved to be 485.2. The theoretical value is 484. The following values were obtained during nitrogen determinations:

$C_{28}H_{24}O_6N_2$. Calculated %: N 5.66, 5.75; Found %: N 5.78.

SUMMARY

Diphenyldianisidine-o,o'-dicarboxylic acid has been synthesized for the first time. In connection with the possibility of using it as a highly sensitive redox indicator in alkaline media it has been called "redoxal". The indicator gives a color change which is instantaneous and contrasting. It has been used for the direct and back titration of quadrivalent vanadium salts with potassium ferricyanide in an alkaline medium. The method described for the determination of vanadium is applicable to the analysis of rocks and iron based alloys.

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* Original Russian pagination. See C. B. translation.

TITRATION OF WEAK BASES IN ACETIC ACID AND IN ITS MIXTURES WITH ACETIC ANHYDRIDE BY MEANS OF AN ANTIMONY ELECTRODE

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Mixtures of acetic acid and acetic anhydride have long been used where acid solvents are required in analytical chemistry practice. It has been shown that addition of acetic anhydride to acetic acid enables tertiary amines to be determined separately in the presence of primary and secondary amines [1, 2]. Russell and Cameron [3] are of the opinion that excess of acetic anhydride in acetic acid significantly increases the acidity of sulfuric acid solutions. Tomiĉek and Heyrovsky [4] have established a relation between additions of anhydride and the potential of the hydrogen electrode in solutions of perchloric acid and sodium acetate. It has been shown [5] that even small additions of acetic anhydride to acetic acid change the acidity of the solutions appreciably, and improve the conditions of acid-base titration. When acetic anhydride is present, it is not only the acidity of sulfuric acid solutions which is increased [3], but also that of perchloric acid [6]. Thus, the increase in acidity is observed for all acids, and is not related – as suggested by Russell and Cameron – to the formation of a mixed anhydride possessing super acid properties.

The increase in acidity of solutions when acetic anhydride is present can be used for improving acid-base titration conditions not only in acetic acid [6-9], but also in other solvents, e.g., in nitromethane [7].

What is still uncertain is the optimum amount of acetic anhydride for acid-base titration in acetic acid. Russell and Cameron, Tomicek and Heyrovsky, and also the authors of [6], have studied the relation between the size of the potential jump and the acetic anhydride content up to 30-40%; it was shown that a significant increase in the potential jump is only observed on addition of the first portions of acetic anhydride, further increases in the amount of acetic anhydride (up to 40%) do not essentially affect the potential jump. Fritz and Fulda [7] found that during titration of a base in nitromethane containing 5, 20, and 50% of acetic anhydride, similar curves were obtained, i.e., addition of more than 5% acetic anhydride does not improve titration conditions.

In this connection we have studied the change in the potential jump of the indicator electrode for solutions of acids and bases, as a function of the solvent composition: from 100% acetic acid to 100% acetic anhydride. Many research workers have indicated that very weak bases whose pK values in water are greater than 12, are not titrated in acetic acid [6, 11-14]. However, on the basis of data on the dissociation constants of bases in acetic acid, and the known Roller ratio [15] $cK_B > 27\ K_i$, it can be concluded that bases which are very weak in water (pK > 12) should be titrated in anhydrous acetic acid, and not only in mixtures of the latter with acetic anhydride. Since excess anhydride in acetic acid essentially changes the acidity of solutions of acids and bases, one might expect an improvement in the titration conditions of very weak bases (urea, caffeine, etc.) in mixtures of acetic acid and acetic anhydride. The possibility of such titration was studied in the work described here.*

* When the work described here had been finished in 1955, articles [8, 9] were published which described the use of a mixture of acetic acid and acetic anhydride for the titration of very weak bases.

It is known from the practice of acid-base titration in nonaqueous media [18], that the glass electrode does not always give good results. This is also true of acid solvents, particularly for mixtures of acetic acid and acetic anhydride. Accordingly, we set ourselves the aim of studying the possibility of using an antimony electrode for acid-base titration in mixtures of acetic acid and acetic anhydride.

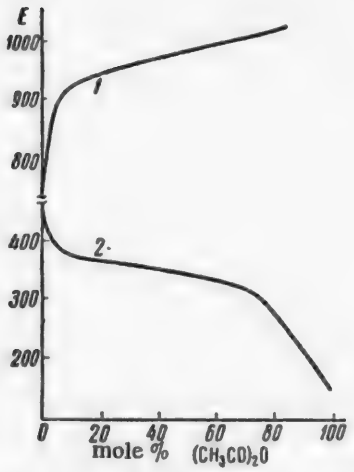

Fig. 1. Change in the emf of the quinhydrone-calomel electrode as a function of the solvent composition: 1) in 0.01 M perchloric acid solution; 2) in 0.01 M pyridine solution.

Experimental Part. Anhydrous acetic acid was prepared from glacial acetic acid by freezing the latter several times, and then distilling it under conditions excluding access to moisture; the final product had a m. p. of 16.6°. Acetic anhydride was prepared by fractionation of the commercial product, the fraction with a boiling point of 139.6° being collected.

The following chemically pure bases were used: pyridine, caffeine, urea, theobromine, and thiourea. Titration was carried out with 0.1 N perchloric acid. Solutions of the bases (0.01 M) and perchloric acid for titration were prepared in anhydrous acetic acid containing 20% acetic anhydride, and in 100% acetic anhydride. During the study of the effect of the composition on the potential jump, 0.01 M solutions of perchloric acid, sodium acetate, and pyridine were used. In the latter case the following circuits were used: quinhydrone – calomel electrodes, and antimony – silver chloride electrodes. Titration was carried out by means of a circuit of antimony – silver chloride electrodes, the silver chloride being immersed in a saturated solution of potassium chloride in 20% acetic anhydride. The antimony electrode used for titration in acetic acid was used earlier by Tomicek and Heyrovsky [4]. Its potential was established rapidly, the titration curves for strong bases (pyridine, sodium acetate) are more symmetrical than those obtained with other electrodes.

All measurements and titrations were carried out at room temperature.

In Fig. 1 is shown the change in emf of the quinhydrone – calomel circuit in 0.01 M perchloric acid and pyridine solutions as a function of the solvent composition. In Figs. 2, 3, 4, and 5 are shown titration curves of bases which are weak in water (pK > 13) in anhydrous acetic acid, and in mixtures of the latter with acetic anhydride and water. When thiourea is titrated in the presence of acetic anhydride two breaks are observed on the titration curve. Experiments showed that separate titration of bases is possible in mixtures of acetic acid and acetic anhydride, or in pure acetic anhydride. During titration the following circuit was set up:

$$Sb \left| \begin{matrix} \text{Base} \\ \text{solution} \end{matrix} \right| \begin{matrix} KCl,\ AgCl \,/\, Ag \\ CH_3COOH + 20\%\,(CH_3CO)_2O \end{matrix}$$

The dissociation constants of the bases were calculated from the titration curves by means of Roller's equation [16], as we did earlier in other papers [5, 17]. The pK values obtained are given in the table.

pK of Weak Bases in Water, Acetic Acid, and Acetic Anhydride

Base	pK in water	pK in acetic acid		pK in acetic anhydride (by titration curves)
		by electroconductivity	by titration curves	
Pyridine	8.85	4.45	4.4	3.7
Caffeine	13.39	—	7.05	—
Urea	13.82	8.3	7.3	5.5
Theobromine	13.89	—	6.2	—
Thiourea	14.96	—	6.89	6.7

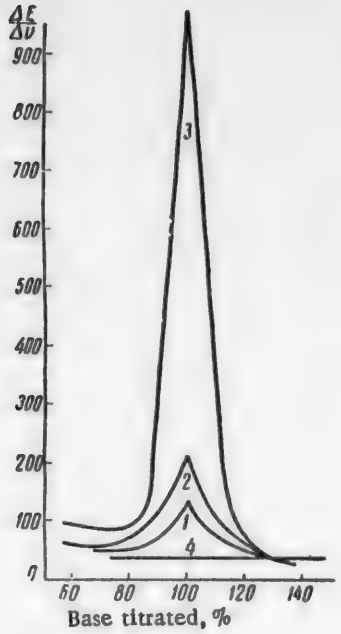

Fig. 2. Curves obtained during titration of 0.01 M urea solution with 0.1 M perchloric acid in mixtures of acetic acid with acetic anhydride and water: 1) in 100% acetic acid; 2) in a mixture of 80% acetic acid and 20% acetic anhydride; 3) in pure anhydride; 4) in acetic acid to which 1% water has been added.

Fig. 3. Curves obtained during titration of 0.01 M caffeine solution with 0.1 M perchloric acid: 1) in 100% acetic acid; 2) acetic acid containing 20% acetic anhydride; 3) in acetic acid containing 0.5% water.

Discussion of Results. An examination of the curves relating potential to solvent composition shows that an essential change in potential occurs on adding the first portions of acetic anhydride to the acetic acid and on the addition of small amounts of acetic acid to acetic anhydride (Fig. 1). On the basis of these curves it can be concluded that for acid–base titration, the best solvent to use is acetic acid to which has been added 10-20%, or, even better, 85-95% acetic anhydride. The most favorable conditions for titration, with respect to the magnitude of the potential jump, are obtained when acetic anhydride is used as solvent.

Even bases which are very weak in water, with a pK in water of 13-15 (urea, caffeine, theobromine, thiourea, etc.) are titrated in anhydrous acetic acid. Consequently, the opposite view of some research workers [11-14] does not seem justified. Apparently, the solvent used by these workers must have contained small amounts of water. As our results have shown, when 1-0.5% of water is added to acetic acid (Fig. 2, Curve 4; Fig. 3, Curve 3) the break on the titration curve disappears. On the other hand, on addition of acetic anhydride to acetic acid, the titration sensitivity increases, and the potential jump returns. The best conditions are obtained in acetic anhydride (90-100%). Some bases, however, e.g., caffeine and theobromine, do not dissolve in acetic anhydride. Accordingly, it is better to use mixtures containing about 20% of the anhydride for these bases, while it is better to use 0.1 M instead of 0.01 M solutions of the bases themselves.

The improvement in the titration conditions on adding acetic anhydride to acetic acid can be explained by a decrease in the ionic product of the medium, and by an increase in the dielectric permeability of the solvent.

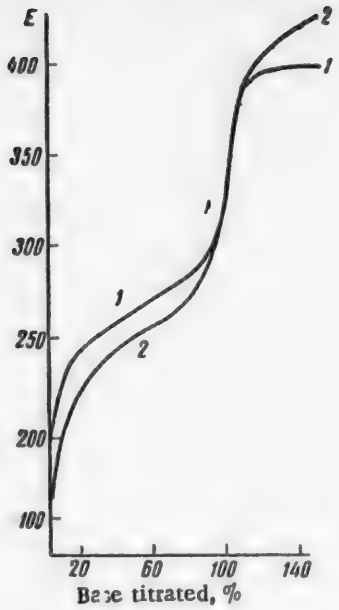

Fig. 4. Curves obtained during titration of 0.01 M theobromine solution with 0.1 M perchloric acid. 1) In 100% acetic acid; 2) in acetic acid containing 20% acetic anhydride.

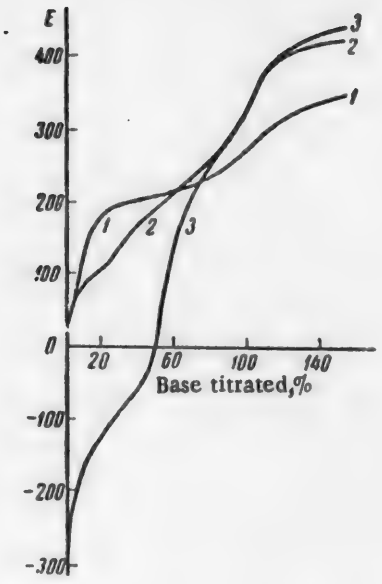

Fig. 5. Titration of 0.01 M thiourea solution with 0.1 M perchloric acid: 1) in 100% acetic acid; 2) in acetic acid containing 20% acetic anhydride; 3) in 100% acetic anhydride.

SUMMARY

The effect of additions of acetic anhydride to acetic acid [from 100% CH_3COOH to 100% $(CH_3CO)_2O$] on the value of the potential jump in solutions of acids and bases has been studied. The curves relating potential and solvent composition make it possible to choose the most favorable solvent composition (a mixture of acetic acid and acetic anhydride) for acid–base titration.

It has been shown that very weak bases – urea, caffeine, theobromine, and thiourea (in water pK > 12) – are titrated in anhydrous acetic acid; when even only small amounts of water are present, the bases indicated are not titrated in acetic acid; addition of acetic anhydride to acetic acid significantly improves the titration conditions of bases. The largest potential jump is observed when pure acetic anhydride is used.

The dissociation constants of pyridine, urea, caffeine, theobromine, and thiourea in anhydrous acetic acid and in acetic anhydride have been determined by means of the titration curves.

It has been shown that an antimony electrode is fully applicable for acid–base titration in acetic acid, and in mixtures of the latter with acetic anhydride.

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* Original Russian pagination. See C. B. translation.

THE PROPERTIES OF ION EXCHANGE MEMBRANES

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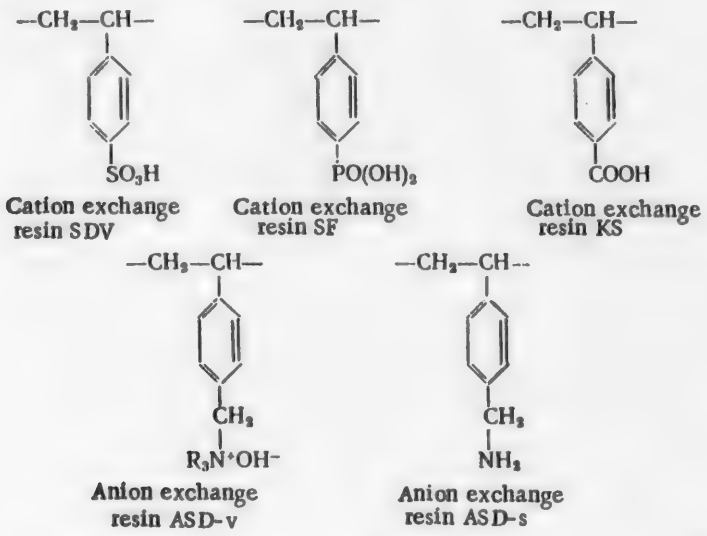
A study of the properties of ion exchange membranes opens up further possible applications of these materials. Electroion exchange setups, provided with ion exchange membranes, are used for desalting or concentrating solutions, and for the separation of cations from anions [1-5]. Electroion exchange methods of separating mixtures of ions, based on differences in the diffusion rate of ions of different valences and dimensions in ion exchange membranes under the influence of a constant electric field, are acquiring more and more interest. In this way, it is possible to separate ions which have such similar properties as magnesium and calcium ions [6], ions of isotopes, sodium and potassium ions, and to produce water enriched with D_2O [7], and to separate organic acids [8]. Ion exchange membranes are also used as electrodes which have a number of advantages of glass electrodes [9]; it is possible by means of ion exchange membranes to extract ions from solutions which are difficult to filter [10]. Ion exchange membranes can be used for the simultaneous extraction of cations and anions from solution.

The diverse uses to which ion exchange membranes are put necessitates an all-around study primarily of the relation between the electrical properties and the structure of the ion exchange resin, the type of ionogenic groups involved, and the ion exchange properties. Such systematic studies have been carried out by Belinskaya and Materova [11]. Analysis of the results have shown that the electrode behavior of the membranes is determined by the type of ionogenic groups in the ion-exchange resin chosen, while the transport number is determined by the concentration of the ionogenic groups in the membrane. Titov [12] has carried out a study on the relation between the properties of the membrane and the capacity, and the degree of swelling of cation-exchange resins. He established that the resistance of sulfonate cation-exchange resins drops with increasing capacity of the cation-exchange resin and its degree of swelling; the transport number and the mechanical stability of the membranes do not depend on the capacity of the cation exchange resin, and drop with increasing degree of swelling. All the studies indicated were carried out on ion-exchange resins whose macromolecules had different structures.

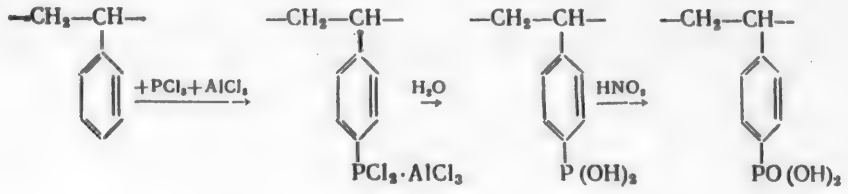
In developing these studies, we have made a comparison of the ion-exchange properties of ion-exchange resins and of the electrical resistance of membranes prepared from these resins. A method of preparing heterogeneous membranes was chosen [9, 13]. Membranes with maximum mechanical stability, chemical stability, and thermal stability can be prepared by using rubber as a binder, particularly chloroprene rubber or carboxylate copolymers of styrene and divinyl. The ion-exchange membranes were prepared under identical conditions. The amount of ion-exchange resin in the membrane was 70%. The ion-exchange resins were ground beforehand in a jet mill until the particle size was 10-40 μ. In order to compare the effect of the type of ionogenic group on the ion-exchange properties of the ion-exchange resin and on the electrical conductivity of the membranes, we considered it necessary to choose ion-exchange resins the structure of whose macromolecules was the same. On this basis, we chose a copolymer of styrene and divinylbenzene which is characterized by the fact that the macromolecules have a distinct structure, and the highest stability in subsequent chemical transformations.

The copolymer chosen had a swelling coefficient of 2.0 in benzene. Methods and conditions for introducing acid and basic groups into the resin were developed specifically for this copolymer. As a result, we obtained a selection of ion-exchange resins in which the macromolecules had the same structure, while they contained different ionogenic groups:

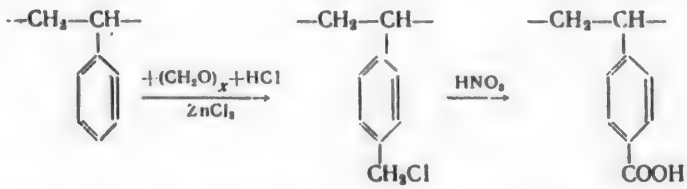


The cation exchange resin SDV was prepared by sulfonating the copolymer with sulfuric acid (sp. gr. 1.84) in the presence of a catalyst at 80-85° for four hours.

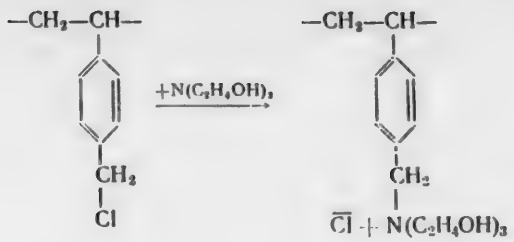
The cation-exchange resin SF was synthesized by phosphorylation of the same copolymer with excess (three moles per styrene link) phosphorus trichloride in the presence of aluminum trichloride (one mole per styrene link). Phosphorylation was carried out for 10 hours at the boiling point of phosphorus trichloride. Breakdown of the intermediate complex was carried out with water: oxidation of the copolymer was carried out by heating the phosphorylated copolymer with nitric acid



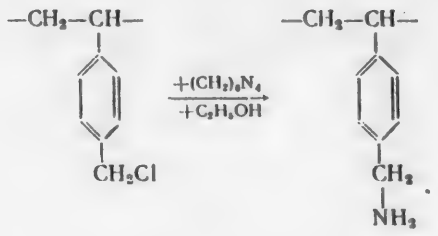
The cation-exchange resin KS was prepared by chloromethylation of the copolymer [14], with subsequent oxidation of the chloromethyl groups in the copolymer. Oxidation was effected by heating the chloromethylated copolymer with nitric acid at a temperature of 70-80° for eight hours:



The anion-exchange resin ASD-v was obtained by replacing the chlorine in the chloromethylated copolymer with triethanolamine. Amination was carried out by heating the chloromethylated copolymer with excess amine at 100° for six hours.



The anion-exchange resin ASD-s was prepared by replacing the chlorine atom in the chloromethylated copolymer of styrene and divinylbenzene, with a primary amine group; this was carried out by the action of the equivalent amount of hexamethylenetetramine at room temperature, with subsequent degradation of the intermediate compound by heating the copolymer with excess ethanol and hydrochloric acid at 60° for three hours.



The properties of the ion-exchange resins synthesized are given in Table 1. The same Table also contains data on the properties of the sulfonated cations exchange resins SBS-1 and SBS-2, and of the average basic anion exchange resin EDE-10P whose macromolecules have a different structure.

TABLE 1

Ion-exchange resin	Acid No. mg-eq/g	Basicity, mg-eq/g	Capacity in 0.1 N NaCl solution, mg-eq/g	Swelling coefficient in water
SDV	4.6	0	4.0	2.1
SF	3.6	0	3.8	1.6
KS	2.3	0	0	1.15
ASD-v	0	2.8	2.1	1.5
ASD-s	0	4.0	0	1.45
SBS-1	2.6	0	2.4	1.25
SBS-2	3.8	0	3.7	2.2
EDE-10P	0	7.5	1.0	2.0

In order to characterize the extent to which the ion-exchange resins ionize at different pH values, results are given in Fig. 1 which were obtained during the potentiometric titration of the cation-exchange resins SDV, SF, SBS-1, KS, while potentiometric titration curves for the anion exchange resins ASD-v, ASD-s, and EDE-10P are given in Fig. 2.

The ion-exchange films were prepared by grinding the cation and anion exchange resins into a powder, they were prepared, respectively, in the hydrogen and hydroxyl forms and mixed with the unfilled raw rubber mixture based on chloropropene rubber. The mixing was carried out in rollers at a temperature not exceeding 30°. The amount of the resin used in all cases was 70% of the total mass. The mixture was calendered until thin films were obtained, the films were then compressed and at the same time vulcanized between heated slabs. Pressing was carried out under a pressure of 10-15 kg/cm^2 and a temperature of 80-100° for 20 minutes.* The properties of the ion-exchange films prepared are indicated in Table 2.

*N. V. Anashkina and V. M. Vinogradov participated in the preparation and study of the ion-exchange films.

Analysis of the results of potentiometric titration, and of the results given in the tables permits one to bring out some regularities. Comparison of the electrical conductivity of films made from SBS-1, SBS-2, and SDV indicates that there is a definite relation between the electrical conductivity of the film and the concentration of ionogenic groups in it, and its degree of swelling. Nevertheless, this relation is not well-defined and is determined to a considerable extent by the structure of the macromolecules of the ion-exchange resin chosen.

TABLE 2

Ion-exchange film	Thickness	Swelling in H_2O, % increase in thickness	Stability limit on stretching, kg/cm²		Specific volume resistance in 0.1 N NaCl, ohm/cm
			dry	swollen	
P-SDV	0.3	37	16.5	8.0	478
P-SBS-1	0.32	18.3	32.0	28.0	1250
P-SBS-2	0.3	22.8	26.0	17.0	430
P-SF	0.28	20.4	17.5	14.0	204
P-KS	0.29	17.0	45.0	47.0	11 680
P-ASD-v	0.34	18.5	25.0	20.0	828
P-ASD-s	0.3	6.8	9.0	4.5	9988
P-EDE-10P	0.31	28.0	7.5	5.0	473

It has not been found possible to give due attention to the effect of the structure of the ion-exchange resin on the electrical properties of the film. Nevertheless, a comparison of the properties of films P-SBS-2 and P-SDV shows that it should be possible to increase the electrical permeability of the diaphragms further by modifying the structure of the ion exchange resin.

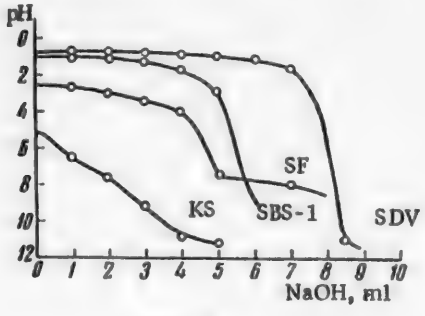


Fig. 1

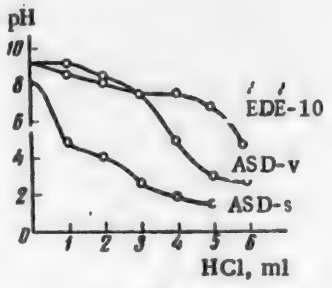


Fig. 2

When the structure of the ion-exchange resin is the same it is easy to follow the relation between the volume resistance of the ion-exchange films and the extent to which the ionogenic groups in the resin are ionized. But, even in this case, comparison of ion-exchange resins with different structures destroys the repeatedly established proportionality in this relationship (e.g., ASD-v and EDE-10P or SBS-2 and SF).

Despite the fact that the concentration of the basic groups in the ion-exchange resin ASD-v is 2.5 times less than that in EDE-10P, its resistance is only twice as much as that of EDE-10P. Preparation of anion exchange resins of the type ASD-v with a higher content of ionogenic groups, and the choice of a more suitable structure for its macromolecules, should enable one to prepare anion exchange resins with the minimum resistance.

The electrical properties of cation exchange films containing phosphate groups have not been described in the literature. Meanwhile, research has shown that films of SF may be of considerable interest for electroion exchange setups, since they have a resistance which is only half that of films of the cation exchange resins SDV and SBS-2. Films containing carboxyl groups and primary amine groups (ion exchange resins KS and ASD-s) have a high resistance and are not suitable as diaphragms in electroion exchange setups.

SUMMARY

Monofunctional ion exchange resins whose macromolecules have the same structure, but which contain different ionogenic groups, have been prepared.

Heterogeneous ion exchange films have been prepared which differ from each other in the type of ionogenic group they contain, or in the structure of the macromolecule of the ion-exchange resin.

It has been established that the electrical properties of ion-exchange films depend not only on the concentration of ionogenic groups in them and the extent to which the latter are ionized, but also on the structure of the macromolecules of the ion-exchange resin chosen.

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AN EXPERIMENT IN THE USE OF A PLASMA GENERATOR FOR THE SPECTROGRAPHIC ANALYSIS OF SILICATES

V. V. Korolev and E. E. Vainshtein

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Recently, Margoshes and Scribner [1], and, independently of them, the authors of the present article [2] turned their attention to the expediency of using a plasma generator [3] as a new, efficient spectrum excitation source, and showed that by means of this source it is possible to achieve a significant increase in the accuracy of the spectrochemical determination of a large number of elements. The present article is devoted to the first results obtained when this source was used for the spectrographic analysis of silicates.

The Design of a Plasma Generator for the Analysis of Solutions. The external appearance and the constructional details of the plasma generator are shown in Fig. 1. The generator consists of a hollow base 1 and a cover 2 cooled by water which passes through a sleeve 3. Between the base and the cover is fitted an insulating glass ring 4. There is an opening in the center of the cover, into which, on thread is fitted a capsule 5 into which a graphite electrode 6 has been fitted beforehand. The cover is fastened by means of an angle bracket 7, a joint 8, and a screw 9 to the triangular plateau 10. In order to change electrodes the cover can be lifted upward by turning the screw around the axis. The base also has an opening with a thread for fitting a gadget carrying the lower carbon electrode 11 to the cell. This gadget consists of a molded socket 12, on the outer surface of which there is a thread; and the socket 13 in which is fitted a bearing 14 with an opening for passing the gas and for setting up the lower electrode. In addition, by means of a socket 15, washer 16, a rubber stopper 17, and spring 18, a separator is fitted to the base of the generator. An arc discharge is excited by direct (short) circuiting of the electrodes, for which purpose the separator 19 and the sleeve 15 connected to it are lifted upward. After the discharge has been excited, all the movable system is returned by means of spring 18 to its original position. Rubber gaskets 20 are used to ensure that the generator is hermetically sealed. For convenience in dismantling the generator, fastening of the cover, and of the base with the glass ring, was achieved by means of three special dowels 21 with molded screws 22. In order to form the aerosol, roughly the same type of glass sprayer fitted with a system of separators as that used in flame photometers is used. In order to lower the extent of condensation of the aerosol on the inner cell walls, a quartz ring 23 is fitted. The arc is fed from a mercury rectifier with rectified current at 270 volt. Cooling gas (argon) is supplied to the generator through the sprayer from a cylinder. The gas pressure is measured with a manometer. A plasma generator of this design enabled us to obtain a plasma stream, bright white in color 40-50 mm long. The dimension of the inner cone* of the plasma stream amounted to 10 mm in length. On introducing water as an aerosol into the plasma, the stream acquired a red color, while the line 4340.5 A of excited hydrogen atoms appeared in the radiation spectrum.

* We use this term arbitrarily by analogy with a flame.

The plasma generator was operated at different current densities and at different pressures of the cooling gas. The optimum conditions were found to be: current, 15-22 amp, and a pressure at the inlet into the sprayer of 0.8-1.2 atm. At lower current densities and at lower gas pressures, ejection of the plasma stream was difficult, and there was observed a break in the sprayer operation. Higher values of current and gas pressure led to overheating of the generator walls and to extinction of the arc discharge.

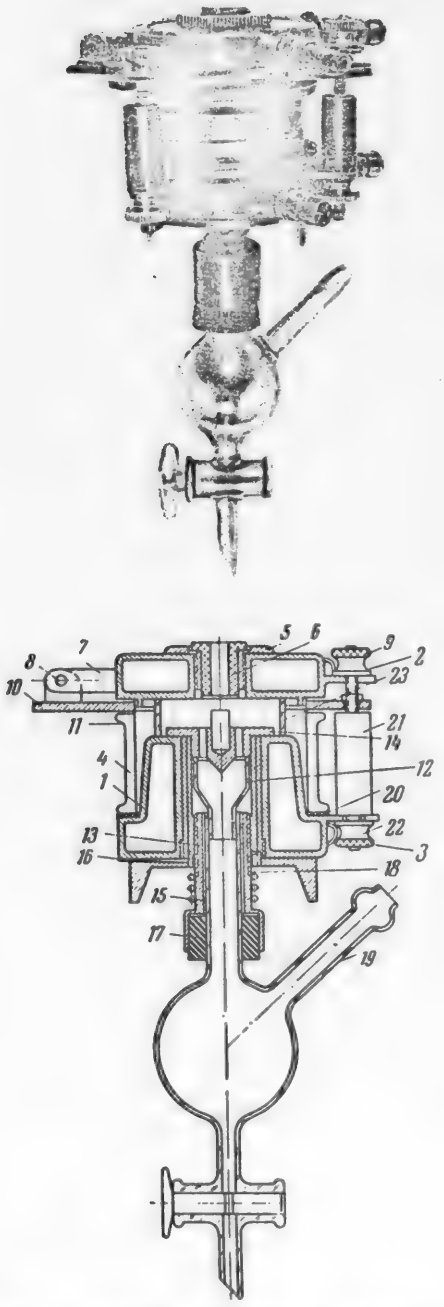

Fig. 1. External appearance and constructional details of the plasma generator used for analysis of solutions.

In a previous communication [2] experimental data were published which enable one to assess the way in which the atoms of certain elements pass into the plasma, and to assess the regularities in the distribution of the excited atoms and ions in the plasma stream. Further work on a large number of elements has shown that on introducing the test solution into the plasma in the form of an aerosol, it is possible to exclude completely the phenomenon of fractional distillation of the elements, and to achieve a high degree of uniformity in the passage of the elements into the plasma stream during analysis (Fig. 2). In Fig. 2, the curves illustrating the passage of Si, Ti, Al, and Fe, obtained during testing of the source, are compared with the corresponding curves obtained during evaporation of the same elements from the sample in the form of a powder in a dc arc and in an impulse arc [4]. It was observed that the degree of uniformity in the passage of the material into the plasma stream could be increased further by adding a small amount of a standard to the test solutions. At the same time, this technique favors an essential increase in the intensity of the whole spectrum, it is, however, accompanied also by some increase in background intensity. In Fig. 3, is shown a group of curves which demonstrate the blackening distribution of the lines of the excited atoms and ions of different elements along the plasma stream. As is evident, for atoms or ions of elements which have low or medium ionization potentials, the curves for changes in blackening of the lines along the plasma stream are characterized by the presence of a distinct maximum. It is located within the limits of the inner cone of the plasma stream, possessing the highest temperature, while the nearer to its base the higher the value of the excitation potential of the line. For lines with the highest excitation potentials, the maximum on the distribution curves, accordingly, almost coincide with the abscissa, i.e., with the base of the plasma stream. Beyond the maximum the paths taken by the distribution curves of the excited atoms and ions along the plasma stream almost coincide for all the elements, and are very near to straight lines. The only exceptions are those elements with very low ionization potentials; for these, at the tip of the plasma stream; there is observed a slower drop in the curve for changes in blackening of the line with distance, than for elements with average values of the excitation potentials.

The high stability of the operation of the generator, the uniformity with which various elements pass into the plasma, and the high degree of similarity in the nature of the distribution of their excited atoms and ions along the plasma stream, ensure high accuracy and reproducibility for spectrographic determination. Moreover, during spectrographic silicate analysis in solution, one can count on appreciably weakening, or avoidance of interference from the mutual effect of the elements on each other, and interference from the base material, and one can analyze samples by means of synthetic standards.

Technique for the Analysis of Silicates. Quantitative determination of the nine basic components of silicate (Si, Ti, Al, Fe, Ca, Mg, Mn, Na, K) is carried out on one aliquot, the contents of the various elements ranging from 0.5 to 80 %. Dissolution of the test material, and determination of the elements are carried out in two stages. During the first stage silicic acid is removed and it is then quantitatively determined gravimetrically [5, 6], while during the second stage the filtrate is analyzed for Ti, Al, Fe, Ca, Mg, Mn, K, and Na.

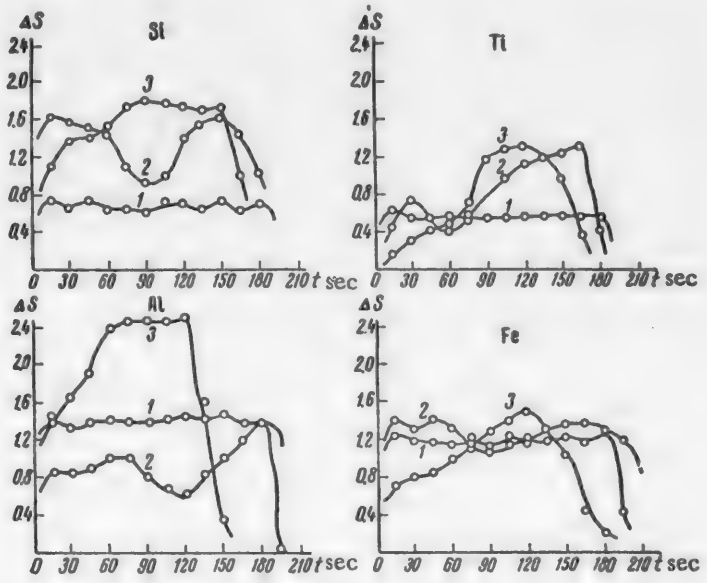

Fig. 2. Change in blackening of the lines ($\Delta S = S_{line} - S_{background}$) of different elements with time, during excitation in the plasma stream of a plasma generator (1), in the plasma of an impulse arc (2), and in a dc arc (3). Silicon on the basis of the 2514 A line, titanium on the basis of the 3653.5 A line, aluminum on the basis of the 3944.0 line and iron on the basis of the 2599.4 A line. The relative arrangement of the curves on the graph is arbitrary.

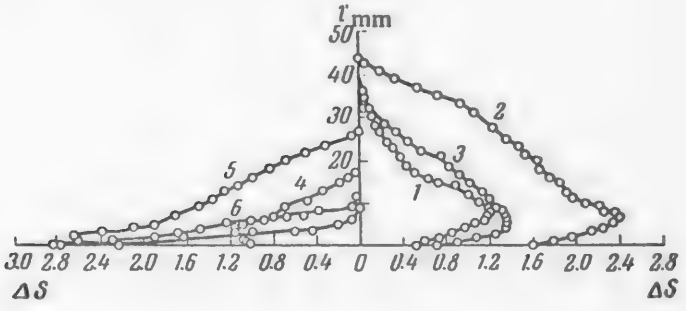

Fig. 3. Change in blackening of the lines ($\Delta S = S_{line} - S_{background}$) of different elements along the plasma stream of the plasma generator. 1) On the basis of the line Na I 588.9 (excitation potential, 3.75 ev); 2) on the basis of the line Al I 3944 (4.02 ev); 3) on the basis of the line Fe I 3020 (4.19 ev); 4) on the basis of the line Fe II 2382.0 (4.82 ev); 5) on the basis of the line Mg II 2802.7 (8.8 ev); 6) on the basis of the line C I 2478.6; 7) on the basis of the line H, 4340.5.

a) Dissolution of the Sample and Determination of SiO_2. A 1 g aliquot of the test silicate is mixed in a platinum crucible with six times its amount of lithium carbonate and is fused with the latter. After cooling, the melt is transferred to a 300 ml beaker, the crucible being rinsed with small portions of hot water. Having covered the beaker with a clock glass, 20 ml of hydrochloric acid sp. gr 1.19 is gradually added through a fine nozzle, and the whole heated on a water bath until the melt has decomposed completely. A little hydrochloric acid sp. gr. 1.19 is added to the crucible in which the fusion was carried out, and the crucible heated in order to dissolve any particles of melt adhering to its side, the contents of the crucible are combined with the main solution. Having rinsed the clock glass, the solution in the beaker is evaporated until moist salts are obtained (not to dryness). To the salts which have formed in the beaker, 30 ml of hydrochloric acid sp. gr. 1.19 is added. Solution plus precipitate are boiled for 10 minutes, after which the beaker is placed on a water bath heated to 70°, the level of the liquid in the beaker being slightly lower than the water level in the bath. When the liquid in the beaker has reached the temperature of the water bath, 10 ml of a 1% gelatin solution is added and the whole thoroughly mixed with a glass rod for 4-5 minutes. The solution is allowed to stand on the bath for a further 10 minutes, after which the beaker is removed from the bath and the liquid allowed to get really cool; after 10 minutes the silicic acid is filtered off through a medium porosity filter paper (white band), and the filtrate collected in a 200 ml beaker. Any particles of silicic acid adhering to the beaker walls are carefully wiped off with pieces of ashless filter paper. The precipitate on the filter is washed with hot water until the washings give no reaction for chloride ions (test with 1% silver nitrate solution). The filter paper plus silicic acid are placed in a platinum crucible, they are dried, carefully ashed, and then calcined in an oven at 1000-1100° to constant weight. The contents of the crucible are washed with water, a few drops of sulfuric acid (1 : 1) is added, followed by 5 ml of hydrofluoric acid and the whole evaporated to dryness. The dry residue is calcined and weighed. The residue in the crucible is fused with 100 mg of lithium carbonate and the melt treated with hot water acidified with hydrochloric acid. The solution obtained is combined with the filtrate left after removal of silicic acid. The filtrate is evaporated to approximately 50 ml and is transferred to a 100 ml standard flask, 6 ml of molybdenum solution is added, the concentration of the latter being 20 mg/ml, and 10 ml of standard; the volume is finally made up to the mark with water.

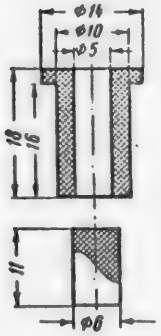

Fig. 4. Shape and size of the electrodes.

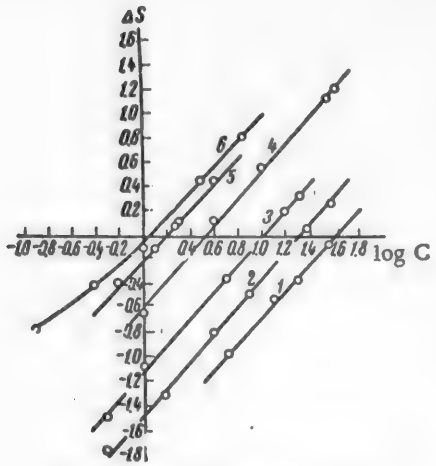

Fig. 5. Calibration curves for the determination of Mg (1), Fe (2), Al (3), Ca (4), Ti (5), Mn (6).

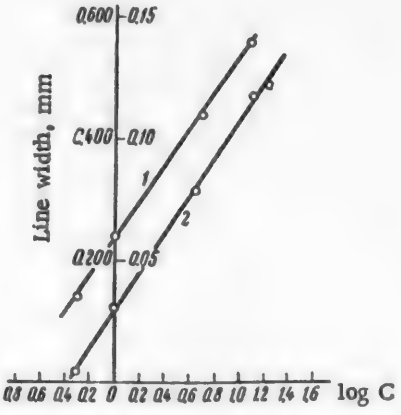

Fig. 6. Calibration curves for the determination of K (2) and Na (1) by the spectral line width method.

b) Spectrographic Analysis of the Filtrate. The filtrate obtained after removing the silicic acid, or a standard solution, converted by means of the sprayer into an aerosol through the system of separators, is transported along rubber tubing into the inner space of the plasma generator, and then into the plasma stream. The

optimum gas pressure at the inlet into the sprayer is 1 atm. Under these conditions the amount of solution used up is 3-4 ml/min. The current is 20 amps. The shape and size of the electrodes are shown in Fig. 4. The interelectrode distance is 4 mm. Both electrodes are replaced after taking three successive spectra, whether of standards or test sample.

Light from the part of the plasma stream located at a distance of about 8-10 mm from the generator nozzle is projected through a one lens system onto the slit of ISP-22 and ISP-51 spectrographs (camera with f = 270 mm). The spectra are photographed on "Spectrographic" plates type II, sensitivity 22 GOST units and on Infrachrome 760 plates. The preliminary exposure time is 15 sec, the main exposure time 60 sec. D-19 developer is used.

Standard solutions, obtained by mixing the appropriate amounts of the chlorides of the test elements and the reference elements, are used for constructing calibration curves.

The analytical lines of the test elements and the appropriate lines of the reference element are given in Table 1. The optimum concentration ranges which are covered by the given pairs of lines are also included. The reference element used for the determination of Ti, Al, Fe, Mg, Ca, and Mn is molybdenum, while lithium is used for the determination of the alkali metals.

TABLE 1

Analytical Lines of the Elements and the Optimum Concentration Range During Determination of These Elements in Silicates

Line of the test element		Reference line		Optimum concentration range of the test element, %
Ti I	3653.5	Mo Mo	3680.6 3208.8	0.1— 2.5
Al I	3944.0	Mo	3208.8	0.5—40.0
Fe II	2599.4	Mo Mo	2616.8 3208.8	0.5—40.0
Ca I	3630.8	Mo	3680.6	3.0—40.0
	4226.7	Mo	4277.2*	0.1— 3.0
Mg II	2779.8 2776.7 2802.7	Mo	2775.4	4.0—40.0 0.1— 4.0
Mn	2801.1	Mo	2775.4	0.1—20.0
Na I	5889.9 5895.9	Mo Li	4760.2 6707.8	0.5—12.0
K I	7664.9 7798.9	Mo Li	4760.2 6707.8	0.5—17.0

* This line can be used when low concentrations of iron are present in the test sample.

The spectrograms obtained were photometrically measured on a MF-2 microphotometer. During determination of the first group of elements the calibration curves were constructed within the coordinates $\Delta S - \log C$ (Fig. 5), while for the determination of Na and K (Fig. 6) the spectral line width method was used [7, 8]. As is evident, in both cases, the calibration curves are linear over a wide concentration range.

The mean square error of a determination of the elements (σ_Σ) obtained after treating the results of 50 parallel determinations, varies within the range 2.5-3.5% (Table 2).

When, using Nalimov's data [9], it is assumed that the values of $\sigma_{phot.}$ and σ_{plate} should be of the order of 1.7 and 2.7%, respectively, for the photographic materials and the developing conditions we used, then the square error related to instability in the operation of the generator under our conditions does not exceed 1.5%. The correctness of the experimental results obtained by the method described was checked by comparing the results of determining the elements by a chemical method and by the spectrographic method (Table 3).

As is evident, the extent to which the experimental results obtained by the two methods agree is completely satisfactory. The question of the mutual influence of the elements on each other during their spectrographic determination by the method described was not specially studied in the work described here. Nevertheless, bearing in mind the results of previous work in this field [7, 8] and the well-known fact that these mutual influences are strongly weakened in work with solutions which are far from being saturated, it may be accepted with a high degree of confidence that such an effect will be almost nonexistent.

TABLE 2

Comparison of Experimental Errors During Determination of Elements by Means of Various Excitation Sources

Source	Standard error of a determination							
	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	Na_2O	K_2O
dc or ac arcs	3.4	6.1	4.5	6.7	—	—	6.0	5.0
Impulse arc	2.7	2.5	2.8	3.3	3.5	3.4	3.5	3.2
Plasma generator	3.2	2.7	2.9	3.4	2.8	3.0	2.8	2.6

TABLE 3

Comparison of the Results of Chemical and Spectrographic Determination of Elements

Sample	1		2		3		4	
Components	Found, %							
	•A	•B	•A	•B	•A	•B	•A	•B
TiO_2	0.42	0.56	0.62	0.61	1.17	1.15	0.76	0.72
Al_2O_3	15.76	15.60	6.85	6.93	18.12	18.63	6.54	6.46
Fe_2O_3	4.19	4.3	3.53	3.54	7.46	7.76	3.32	3.29
CaO	4.77	4.67	0.38	0.41	3.14	3.06	0.15	0.15
MgO	1.92	2.05	0.40	0.41	3.95	3.98	0.52	0.51
MnO	0.1	0.1	0.07	0.07	0.06	0.06	0.28	0.28
Na_2O	5.02	4.95	0.08	0.10	0.01	Not det.	0.01	Not det.
K_2O	1.99	2.08	0.36	0.38	6.55	6.35	0.94	0.92

• A = Chemical method, • B = Spectrographic method.

The authors wish to thank N. I. Korolev for help in the experimental work.

SUMMARY

A design for a plasma generator which can be used for the analysis of solutions is described; new results have been obtained which indicate a high degree of uniformity in the passage of elements into the source plasma, and which indicate the characteristic nature of the distribution of excited atoms and ions of certain elements (Na, Al, Fe, Mg, Si, C, and H) in the plasma stream.

A new spectrochemical method has been developed for the quantitative determination of from 0.5 to 80% of Si, Ti, Al, Fe, Ca, Mg, Mn, Na, and K in silicates, with an average square error of 2.5-3.5%.

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THE USE OF THIOSEMICARBAZIDE AND ITS PHENYL DERIVATIVES IN ANALYTICAL CHEMISTRY.

SPOT AND NONDESTRUCTIVE TESTS FOR COPPER

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Thiosemicarbazide and its phenyl derivatives* are used in analytical chemistry for the detection and determination of certain metals [1-8]. Earlier [2] one of us developed a method for the photocolorimetric determination of copper by means of thiosemicarbazide. We thought it would be interesting to establish the effect of the introduction of various substituents into the thiosemicarbazide molecule, on the selectivity and sensitivity of this reaction. One should expect that the nature of the way in which the reaction proceeds between copper ions and thiosemicarbazide on the one hand, and between copper ions and the substituted thiosemicarbazides on the other, will differ somewhat as a result of the replacement of the hydrogen in the molecule of the reagent by phenyl and other groups. It might be expected in such a case that the sensitivity and selectivity of the reaction in the second case will be greater than in the first. The acidity of the medium might also be significant, since, depending on the latter, various tautomeric forms of the compounds of thiosemicarbazide and its derivatives may be formed with copper ions.

In this connection we therefore studied 2-methyl-, 4-methyl-, 2,4-dimethyl-, 1-phenyl-, 4-phenyl-, and 1,4-diphenylthiosemicarbazides as reagents for copper.

Unsubstituted thiosemicarbazide gives with copper ions at pH 0-4 in nitric, hydrochloric, and sulfuric acid solutions, a dark blue colored compound which is soluble in water and sparingly soluble in organic solvents. The alkyl derivatives of thiosemicarbazide also give blue colored compounds under the same conditions, but the sensitivity of the reaction of these derivatives with copper is no higher than that of thiosemicarbazide itself. At pH 4-12, the alkyl substituted derivatives of thiosemicarbazide, like thiosemicarbazide itself, form yellow-brown colored compounds with copper ions. We did not study the alkyl substituted derivatives of thiosemicarbazide further.

A chemical analysis of the products formed by the interaction of thiosemicarbazide with copper ions in acid and alkaline media showed that their composition is not the same. For a compound isolated earlier by one of us [2] from an acid solution, the copper content was found to be 18.6% instead of the theoretical value of 18.5%. Physicochemical studies showed that the ratio of copper to thiosemicarbazide in this compound was 1:2, while magnetometric measurements established the presence of cupric ions only. Appropriate qualitative reactions and chromatographic experiments showed that this compound is an electrolyte. The product formed

* We only learned of the detection and determination of copper by 1,4-diphenyl thiosemicarbazide [7] when the work described here had been completed. Since the results we have obtained extend and supplement available information, we decided that it would be useful to publish them.

by the interaction of thiosemicarbazide with copper ions in alkaline media is not an individual material. The magnetic moment of this compound corresponds to divalent copper and is 1.46 M_0 (for univalent copper it is 0, while for divalent copper which is paramagnetic, it is 1.75 M_0). The copper content of this product was found to be 58.8% and the sulfur content 41.6%. The product obtained is insoluble in water, and, apparently, is a complex nonelectrolyte. The composition of the compound formed by the interaction of thiosemicarbazide with copper ions in an alkaline medium was not studied by physicochemical methods.

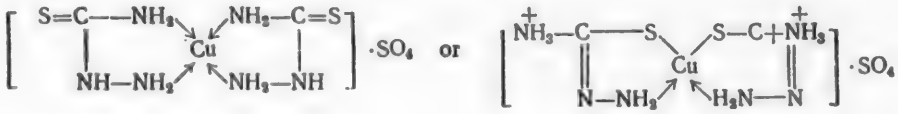
1-Phenylthiosemicarbazide, which was suggested as a reagent for copper by Naito and Takahashi [5], gives with copper ions at pH 0-4, a blue colored compound, while at higher pH values the compound formed is green in color. It behaves up to a certain extent in the same way as thiosemicarbazide. The compound formed between 1-phenylthiosemicarbazide and copper ions in an acid medium, is sparingly soluble in water, and is fairly soluble in acetic acid and organic solvents.

4-Phenylthiosemicarbazide forms a green colored compound with copper ions. In very dilute solutions the green color of this compound is preserved over a wide pH range (0-12). In more concentrated solutions, at pH greater than 2, a precipitate of pale violet color is formed, which is insoluble in water and ethanol, and sparingly soluble in organic solvents and mineral acids.

Using the isomolar series method it was shown that in acid media, 1-phenylthiosemicarbazide and 4-phenylthiosemicarbazide react with copper ions in the molar ratio of 1 : 2. These compounds were not analyzed chemically.

1,4-Diphenylthiosemicarbazide at pH 0-12, forms a green colored compound with copper ions. This compound is sparingly soluble in water, but is readily soluble in organic solvents: benzene, chloroform, carbon tetrachloride, ethyl, amyl, and isoamyl alcohols, toluene, and acetone. The compounds formed between 1,4-diphenylthiosemicarbazide with copper ions in acid (pH 1-2) and alkaline (pH 9-10) solutions were isolated in a crystalline state, and proved to be identical. When these compounds were prepared from sulfuric acid solutions, it was found that they did not contain the sulfate ions, this was proved by the absence of a precipitate on testing with barium nitrate. They were also free from Cl^- and NO_3^- when prepared from hydrochloric and nitric acid solutions. Apparently, 1,4-diphenylthiosemicarbazide forms only one compound with copper ions, this compound being probably a complex nonelectrolyte. Chemical analysis established that the copper content of this compound is 13.5% while the sulfur content is 12.02%; these figures tie in most closely with the formula $Cu(C_{13}H_{12}N_3S_2)$ (calculated values: 11.6% Cu and 11.67% S). This ratio was confirmed by measuring the optical density of isomolar mixtures of aqueous-alcoholic solutions of 1,4-diphenylthiosemicarbazide and aqueous solutions of cupric sulfate, and also of mixtures of solutions with varying concentrations of one of the components, on a SF-4 spectrophotometer at varying wavelengths.

The sulfate of cupric thiosemicarbazidinate, isolated from an acid solution, may have the following structure



In order to choose between one structural formula and the other, infrared absorption spectra were taken of thiosemicarbazide, 1,4-diphenylthiosemicarbazide and of their compounds with copper, on a IKS-12 spectrophotometer, in the region characteristic for the absorption frequency of the thioureide group $-N=C=S$. On comparing these spectra it was established that bands with a frequency of 1540 cm^{-1} are present in the spectra of thiosemicarbazide and 1,4-diphenylthiosemicarbazide, these bands obviously belong to the thioureide group (according to published data the characteristic frequency of this group lies within the range 1470-1600 cm^{-1}). The absorption spectra of the compounds of thiosemicarbazide and 1,4-diphenylthiosemicarbazide with copper do not contain any bands in the region indicated. The disappearance of the absorption bands indicated testifies to some extent that the sulfur atom participates in the formation of the bond with the copper ion.*

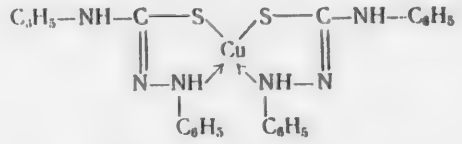
* The infrared absorption spectra of thiosemicarbazide and 1,4-diphenylthiosemicarbazide, and also of their compounds with copper, were taken by L. F. Trefilova.

Taking into account all that has been said above, and also the opinions of Kuznetsov [9], Irving [10], Toropova [12] and other research workers on the structure of complex compounds of metallic ions with organic compounds containing sulfur, the second structural formula given above would appear to be most likely one for cupric thiosemicarbazadinate sulfate.

Formulas analogous to that of cupric thiosemicarbazadinate sulfate can, presumably, be ascribed to the compounds of 1-phenyl- and 4-phenylthiosemicarbazide with copper ions when isolated from acid solutions.

The properties and composition of the compounds of thiosemicarbazide, 1-phenylthiosemicarbazide, and 4-phenylthiosemicarbazide with copper ions, isolated from alkaline solutions were not studied.

As for the compound of 1,4-diphenylthiosemicarbazide with copper ions, it is presumably a complex nonelectrolyte (inner complex compounds). The properties of this compound are in good agreement with the formula:



1-Phenyl, 4-phenyl-, and 1,4-diphenylthiosemicarbazides, in view of the presence in their molecules of phenyl groups in addition to the thio group, could presumably be more sensitive reagents for copper ions than thiosemicarbazide and semicarbazide. Experiments which were carried out showed that in fact the sensitivity of reactions involving the phenyl substituted thiosemicarbazides is higher than that with thiosemicarbazide and semicarbazide. Using organic solvents for extracting the compounds formed, the sensitivity is $5.0 \cdot 10^{-8}$ g/ml for 1,4-diphenylthiosemicarbazide, $5.0 \cdot 10^{-6}$ g/ml for 4-phenylthiosemicarbazide, and $5.0 \cdot 10^{-7}$ g/ml for 1-phenylthiosemicarbazide. The sensitivity of the analogous reactions with thiosemicarbazide and semicarbazide is $5.0 \cdot 10^{-6}$ and $5.0 \cdot 10^{-4}$ g/ml, respectively.

On adding a solution of thiosemicarbazide to a solution of copper semicarbazadinate, the color changes from light-blue to the blue-violet characteristic of copper thiosemicarbazadinate. By the action of 1-phenylthiosemicarbazide on a solution of copper thiosemicarbazadinate, the color changes into a dark-blue characteristic of copper 1-phenylthiosemicarbazadinate. On adding solutions of 4-phenylthiosemicarbazide or 1,4-diphenylthiosemicarbazide to a solution of copper 1-phenylthiosemicarbazadinate, the color changes to green characteristic for copper 4-phenyl- and 1,4-diphenylthiosemicarbazadinates (when a solution of the second reagent is used, and at a sufficiently high concentration of 1-phenylthiosemicarbazide in solution, a green precipitate is rapidly formed). On mixing a solution of sodium ethylenediaminetetracetate (EDTA-Na) with a solution of copper 1,4-diphenylthiosemicarbazidinate the green color slowly changes to a bright-blue, characteristic for copper ethylenediaminetetracetate.

On the basis of the results given above, it is possible to compile a practical series of copper carbazadinates, in which each of the preceding members is less stable than the subsequent member:

$$[Cu(SC)_2]^{2+}, [Cu(TSC)_2]^{2+}, [Cu(1\text{-}FTSC)_2]^{2+}, [Cu(4\text{-}FTSC)_2]^{2+}, [Cu(1,4\text{-}DFTSC)_2]$$

1,4-Diphenylthiosemicarbazide gives stable, and, in some cases, sparingly soluble compounds, not only with copper, but also with silver, mercury, zinc, cadmium, iron, gold, platinum, palladium, iridium, rhodium, and ruthenium; only platinum of the noble metals forming a green colored compound. They are readily extracted by organic solvents, but the reaction of 1,4-diphenylthiosemicarbazide with the ions of these metals is less sensitive than its reaction with copper. Small amounts of the cations of the metals indicated do not interfere with detection of copper, large amounts depress the sensitivity of detection somewhat. Copper can be detected in the presence of silver and mercury at a ratio of Cu : Me = 1 : 1000, while in the presence of gold, palladium, ruthenium, osmium, rhodium, iridium, platinum and rhenium, copper can be detected at a ratio of Cu : Me = 1 : 30. Interference from large amounts of iron can be removed by using sodium fluoride or phosphate. The majority of anions, with the exception of intensely colored ones, does not interfere with copper detection. Concentrated nitric and perchloric acid destroy the compounds formed between metal ions and 1,4-diphenylthiosemicarbazide.

The listed properties of the inner complex compound formed during the interaction of cupric ions with 1,4-diphenylthiosemicarbazide favorably distinguish this reagent from thiosemicarbazide and 1-phenylthiosemicarbazide, and some other compounds which have been suggested for the detection and determination of copper.

Preparation of 1,4-Diphenylthiosemicarbazide and its Compound with Cupric Ions. Walther's method [13], somewhat improved by us, was used for synthesizing 1,4-diphenylthiosemicarbazide.

6.9 g (0.03 mole) of thiosemicarbazide (diphenylthiourea) and 4 ml (4.3 g or 0.04 mole) of phenylhydrazine were boiled in 50 ml of alcohol in a flask fitted with a reflux condenser for four hours. After cooling the reaction mixture, the precipitate which separated out was filtered and washed with alcohol. The 1,4-diphenylthiosemicarbazide prepared in this way appeared as shining prisms with a m. p. of 177° (published m. p. 176-177°). Yield 6.7 g (92% of theory).

The compound of 1,4-diphenylthiosemicarbazide with copper was obtained both in acid and in alkaline solutions. An aqueous solution of a copper salt was mixed with a solution of 1,4-diphenylthiosemicarbazide in concentrated acetic acid. The shining green crystals which thereby separated out were filtered off, washed with alcohol and dried between sheets of filter paper and stored in a desiccator over sulfuric acid. During isolation of the compound of 1,4-diphenylthiosemicarbazide with copper ions from an alkaline solution, an alcoholic solution of 1,4-diphenylthiosemicarbazide was added to an aqueous-ammonia solution of a copper salt; the subsequent procedure was the same as in the previous instance.

Methods of Detecting Copper by Means of 1-Phenyl- and 1,4-Diphenylthiosemicarbazide. To 0.2-0.3 ml of the test solution is added 1-2 ml of a saturated alcoholic or acetic acid solution of reagent (1-phenylthiosemicarbazide or 1,4-diphenylthiosemicarbazide) and the whole mixed. If, at this stage a precipitate is formed, the volume of reagent added is increased 2-3 times, or the corresponding amount of ethanol is added. The appearance of a green color (when 1,4-diphenylthiosemicarbazide is used) or a blue color (when 1-phenylthiosemicarbazide is used) testifies to the presence of copper in the test solution. Under these conditions, the sensitivity of the detection of copper in the presence of other cations amounts to $5.0 \cdot 10^{-6}$ g/ml for 1,4-diphenylthiosemicarbazide and $5.0 \cdot 10^{-5}$ g/ml for 1-phenylthiosemicarbazide.

Spot Detection of Copper in the presence of other cations is carried out as follows. 0.01-0.005 ml of test solution is placed by means of a capillary on a sheet of filter paper. 0.03-0.06 ml of reagent solution is placed by means of another capillary in the center of the still moist spot of test solution. When copper is present a green ring is formed between the center and the periphery of the spot. When the test solution contains mercury and gold a large excess of reagent must be used, this is done by putting two or three spots of reagent solution on the center of the moist spot. In this case, in addition to the green ring, a brown color appears at the spot center; this means that it is possible to detect copper, mercury, and gold, simultaneously. The sensitivity of the detection of copper in the presence of the other cations by the spot technique, using 1,4-diphenylthiosemicarbazide, is $6.0 \cdot 10^{-7}$ g/ml, while in the absence of the cations, the sensitivity is $1.0 \cdot 10^{-7}$ g/ml.

Nondestructive Detection of Copper by means of 1,4-diphenylthiosemicarbazide was carried out on zinc, nickel, ferrous, and gold alloys. On the surface of the alloys which has been cleaned beforehand is placed 2-3 drops of nitric acid (1 :1) for zinc and ferrous alloys, or the same amount of a mixture of nitric and hydrochloric acids (1 :1) for gold alloys. After the reaction has ceased, the solution on the alloy's surface is transferred to a porcelain crucible or basin. The alloy surface is washed with 2-3 drops of water and the wash water combined with the solution in the crucible. 1-2 drops of nitric acid is added to the solution in the crucible and the whole evaporated almost to dryness on a hot plate. To the residue is added 1-2 drops of hydrochloric acid and the volume of the solution made up to 1-2 ml with water. The solution is transferred to a test tube and 1-2 ml of reagent solution added. When a precipitate forms, 1-2 ml of ethanol is added. When copper is present a green color is formed.

During analysis of ferrous alloys, iron is masked by addition of sodium fluoride, while during the analysis of nickel alloys the solution is diluted with water to weaken the green color of the nickel salts. The test materials used for this study were zinc alloys containing 0.5 and 0.94% copper, a nickel alloy containing 0.54% copper, a carbon steel containing 0.33% copper, and a gold alloy containing 30.3% copper.

We wish to thank I. Ya. Postovskii for valuable advice in carrying out the work described here.

SUMMARY

A study has been made of the reaction of copper ions with certain substituted thiosemicarbazides.

Structural formulas are suggested for the compounds of copper with thiosemicarbazide and 1,4-diphenylthiosemicarbazide.

Optimum conditions have been established for carrying out the reactions with phenyl substituted derivatives of thiosemicarbazide, and the sensitivity of these reactions have been determined in pure solutions of copper salts, and in the presence of other elements.

Methods have been developed for detecting copper in zinc, nickel, gold, and ferrous alloys.

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SEPARATION AND DETERMINATION OF GALLIUM BY MEANS OF DIANTIPYRYLPROPYLMETHANE

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For the determination of comparatively large amounts of gallium, the latter is usually precipitated with ammonia, ammonium sulfite, camphoric acid, cupferron, and some other reagents, and it is finally weighed as Ga_2O_3 [1]. As a rule, the precipitates formed under these conditions are difficult to filter. In addition, many of the forms in which this element is weighed have unfavorable conversion factors. Other methods of precipitating gallium, e.g., in the form of its ferrocyanide, 8-hydroxyquinolate $(C_9H_6ON)_3Ga$, possess low selectivity and are only of importance for the determination of gallium in its pure salts, or after its separation, e.g., by extraction with diethyl ether from 5-6 M HCl.

Gallium is extracted in the form of basic compounds $HGaCl_4 \cdot x$ Org (where Org is the molecule of an oxygen-containing organic solvent).

The aim of the work described here, was to carry out a systematic study of the possibility of using precipitation of gallium by means of diantipyrylpropylmethane, for the separation and quantitative determination of this element. Diantipyrylpropylmethane has been used earlier [2] for the gravimetric determination of thallium in the presence of many elements including zinc, cadmium, copper, indium, and aluminum. Interference on the part of gallium was noted at the time.

Experiments showed that gallium starts to be precipitated by diantipyrylpropylmethane from 3 M HCl, it is precipitated quantitatively from 5.5-6 M HCl. Diantipyrylmethane and diantipyrylmethylmethane do not precipitate gallium quantitatively from hydrochloric acid solutions.

In order to determine the composition of the compound which is formed in hydrochloric acid solutions (6 M HCl) of gallium salts on adding diantipyrylpropylmethane, the precipitate obtained was filtered off and recrystallized from acetone; during this process the material separated out in the form of a colorless oily liquid which slowly crystallized on standing. Chlorine was determined by precipitation with silver nitrate from an aqueous-acetone solution, and weighing as AgCl, while gallium was determined by complexonometric titration with 1-(2-pyridylazo)-2-naphthol as indicator. In this latter instance an aliquot of the material was dissolved in a mixture of acetone and water (1 : 10), 2-3 ml of a 5% solution of tartaric acid was added, this was followed by ammonium acetate until the pH was 4.5-5, the solution was heated to 70-80° and gallium titrated with 0.01 M sodium ethylenediaminetetracetate in the presence of a few drops of a 0.1% solution of 1-(2-pyridylazo)-2-naphthol in methanol (until the color changed from red to pure yellow).

Analytical results showed that gallium is precipitated in the form of a compound whose composition corresponds to the formula $C_{28}H_{30}O_2N_4 \cdot HGaCl_4$.

Found %: Cl 22.09, 21.76; Ga 10.84, 10.97. $C_{28}H_{30}O_2N_4 \cdot HGaCl_4$. Calculated %: Cl 22.05; Ga 10.84.

In order to determine gallium quantitatively in the form of $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$, to the test solution (we used a solution of gallium chloride obtained by dissolving an accurately weighed aliquot of spectrographically pure metallic gallium in hydrochloric acid) was added a 1% solution of diantipyrylpropylmethane in acetic acid (1 : 10), at the rate of 1 ml per mg of gallium, to the solution was then added, with stirring, an equal volume of hydrochloric acid (sp. gr. 1.19). Thus, the final hydrochloric acid concentration was 5.5-6 M. The white flocculent precipitate which formed, and which readily coagulated on stirring, was filtered off through a No. 3 glass crucible, and was washed with 6 M HCl containing 0.05% of the precipitant, and then with 6 M HCl. The precipitate was dried to constant weight at 100-110° (at this temperature the precipitate melts without decomposition). The conversion factor to gallium is 0.1084. The method gives results which are fully satisfactory with respect to accuracy. (Table 1); in addition, it is simple to carry out, and takes little time since the precipitate is readily and rapidly filtered.

TABLE 1

Gravimetric Determination of Gallium in the Form of $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$

Ga, mg		Error	
taken	found	mg	%
3.37	3.39	+0.02	+0.6
3.37	3.36	−0.01	−0.3
3.37	3.34	−0.03	−0.9
4.62	4.53	−0.09	−2.0
4.62	4.67	+0.05	+1.0
8.44	8.51	+0.07	+0.8
8.44	8.40	−0.04	−0.5
8.44	8.45	+0.01	−0.1
16.87	16.80	−0.07	−0.4
16.87	16.60	−0.27	−1.6

TABLE 2

Determination of Gallium in the Presence of Foreign Elements

Ga, taken, mg	Added, g		Ga found, mg	Error	
				mg	%
8.44	0.5	$CuSO_4 \cdot 5H_2O$	8.39	−0.05	−0.6
8.44	1.0	$CuSO_4 \cdot 5H_2O$	8.32	−0.12	−1.3
3.37	2.0	$Zn(CH_3COO)_2 \cdot 2H_2O$	3.44	+0.07	+2.0
3.37	3.0	$Zn(CH_3COO)_2 \cdot 2H_2O$	3.33	−0.04	−1.2
3.37	0.17	In	3.36	−0.01	−0.3
3.37	2.0	$Al(NO_3)_3 \cdot 9H_2O$	3.46	+0.09	+2.7
3.37	3.0	$Cd(NO_3)_2 \cdot 4H_2O$	3.40	+0.03	+0.9
3.37	4.5	$Cd(NO_3)_2 \cdot 4H_2O$	3.28	−0.09	−2.7
8.44	3.0	$Al(NO_3)_3 \cdot 9H_2O$	8.40	−0.04	−0.5
8.44	2.0	$Al(NO_3)_3 \cdot 9H_2O$	8.72	+0.28	+3.3
8.44	1.0	$Ni(NO_3)_2 \cdot 6H_2O$	8.36	−0.08	−1.0
3.37	2.0	$Ni(NO_3)_2 \cdot 6H_2O$	3.27	−0.10	−3.0
8.44	3.0	$MnCl_2 \cdot 4H_2O$	8.38	−0.06	−0.7
16.87	2.5	$MnCl_2 \cdot 4H_2O$	16.63	−0.24	−1.4
3.57	3.0	$MgCl_2 \cdot 6H_2O$	3.40	+0.03	+0.9

The suggested method possesses a high selectivity, since many elements do not interfere, they include: zinc, cadmium, copper, aluminum, nickel, manganese, magnesium, indium, cobalt, bismuth, and other elements (Table 2). Tl^{3+} and Fe^{3+} interfere.

Accordingly, the method can be used both for isolating gallium and separating it from accompanying elements. Trivalent iron must be reduced to the divalent state.

After gallium has been separated as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$ its determination can be finished complexonometrically: the precipitate is filtered off, washed as indicated above, and then washed off the filter with water (50-70 ml), to the solution is added a few ml of a 5% tartaric acid solution, and the pH adjusted to about 5 with ammonium acetate; it is finally titrated, after warming it to 70-80°, in the presence of 1-(2-pyridylazo)-2-naphthol until the color of the solution turns from rose to yellow. The method gives satisfactory results (Table 3).

TABLE 3

Complexonometric Determination of Gallium After It Has Been Separated as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$

Ga taken, mg	Added, g	Ga found, mg	Error, mg
3.37	—	3.36	—0.01
3.37	—	3.39	+0.02
8.44	—	8.37	—0.07
16.87	—	16.99	+0.12
8.44	0.25 $Bi(NO_3)_3 \cdot 5H_2O$	8.55	+0.11
8.44	0.50 $Bi(NO_3)_3 \cdot 5H_2O$	8.37	—0.07
8.44	1.0 $CoSO_4 \cdot 7H_2O$	8.43	—0.01
3.37	1.0 $CoSO_4 \cdot 7H_2O$	3.26	—0.11
3.37	0.437 In	3.36	—0.01
3.37	0.604 In	3.45	+0.08

SUMMARY

A description is given of a simple method for the isolation and separation of gallium from accompanying elements; the method is based on the precipitation of gallium . As $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$ from 5.5-6 M HCl by means of diantipyrylpropylmethane. Either a gravimetric finish can be used, in which the gallium is weighed as $C_{26}H_{30}O_2N_4 \cdot HGaCl_4$, or the gallium can be determined complexonometrically, by titrating the gallium in the precipitate using 1-(2-pyridylazo)-2-naphthol as indicator.

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• Original Russian pagination. See C. B. translation.

DETERMINATION OF THE INDIUM CONTENT OF SPHALERITES BY RADIOACTIVATION ANALYSIS

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In papers [1-4] which have been published on the determination of indium in various samples by means of the activation method, radiochemical methods of separating indium from other elements are used in the main, these entail difficult and long operations. In this connection we have attempted to develop a technique for the determination of indium in sphalerites by direct measurement of the energy spectra of the test sample by means of a scintillation γ-spectrometer.

Development of quantitative methods for determining from hundredths to several tenths of a percent of indium in sphalerites is of practical importance. The basis of the technique is to obtain radioisotopes of indium by means of (n, γ) reactions. In Table 1 are given the energy characteristics of the elements which are present in sphalerites.

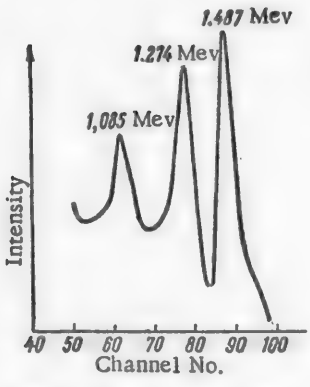

Fig. 1. The γ-radiation spectrum of the standard indium isotope-116.

The setup which we used consists of the following main parts: a) a vertical lead housing of special design (in which is found the spectrophotometer monocrystal NaI (Tl) which is 40 mm in diameter and 38 mm in length, and a photoelectronic multiplier type FEU-1S plus divider which is optically connected to it); b) a single channel amplitude analyzer with an amplifier; c) a counting setup; d) a stabilized high voltage rectifier.

The activated sample contained in a special cassette (cylindrical in shape) of organic glass was fitted onto the crystal in the lead housing. The electrical impulses from the photoelectronic multiplier passed (through a cathode repeater) onto the input of the amplifier. The analyzer channel was set up in the region of the photopeak with an energy of 1.273 Mev on the scale of the energy γ-spectrum of indium-116 (Fig. 1) for a channel width of 5 volt. The impulses were counted by a type PS-10,000 type counting setup. Prior to measurement of the activity of samples, the analyzer scale was calibrated on the basis of the energy photopeaks of the γ-radiation of the isotopes iodine-131, cobalt-60, cesium-137, and zinc-65. The energy scale of the analyzer in the energy range 0.3 to 1.5 Mev proved to be linear (Fig. 2).

In order to calculate the values of the activity of elements which enter into the composition of sphalerite, the results in Table 1 were used; their drop in activity curves (Fig. 3) were then constructed. The activity was calculated by means of the formula

$$\dot{I} = n\nu\sigma N\left(1 - e^{-\frac{0{,}693t}{T}}\right),$$

TABLE 1

Nuclear Characteristics of Elements Present in Sphalerite

Element	Isotope, distribution, %	Effective activation cross section by slow neutrons, b	Radioactive isotope	Half life period	Nature of the radiation β, γ	β-Radiation energy, Mev	γ-Radiation energy, mev	Yield of γ-quanta per 100 decays, %	Conc. of elements in the sample, %	Calc. activation I in arbitrary units for irradiation time of 3 hrs 30 min.	Log I
Sulfur	S^{34} (4.2)	0.26	S^{35}	87 days	β^-	0.167	none	—			
						4.3 (10%)			33		
16^S	S^{36} (0.016)	0.14	S^{37}	5 min	β^-,	1.6 (90%)	3.1	90.0		$2 \cdot 10^8$	2.9956
Zinc	Zn^{64} (48.9)	0.5	Zn^{65}	250 days	β^+,	0.325 (1.7%)	1.12	45.5			
							0.51	3.0			
30^{Zn}	Zn^{68} (18.6)	0.1	Zn^{69m}	14 hrs	β^-,	0.92	0.44	95.5	66.6	$5.3 \cdot 10^4$	10.8780
	Zu^{68} (18.6)	1.0	Zn^{69}	52 min	β^-	0.9	none	—		$1.97 \cdot 10^6$	14.4986
Gallium	Ga^{69} (60.2)	1.4	Ga^{70}	20 min	β^-,	1.6	1.036	0.8	0.1	$1.2 \cdot 10^5$	11.6962
							0.174	0.5			
71^{Ga}	Ga^{71} (39.8)	3.4	Ga^{72}	14 hrs	β^-,	3.15 (9%)	0.84	96.7		$1 \cdot 10^9$	8.5172
						2.5 (8%), 1.5	2.2				
						0.9; 0.6	0.63	21.4			
Germanium	Ge^{70} (20.4)	3.0	Ge^{71}	11 days		1.137 (89%)				$2.6 \cdot 10^8$	7.8633
	Ge^{74} (36.6)	0.45	Ge^{75}	82 min	β^-	0.614 (15%)	none	—	0.1	$2 \cdot 10^9$	7.6009
32^{Ge}	Ge^{76} (7.8)	0.2	Ge^{77}	12 hrs	β^-	2.196	0.6				
						1.379				$5.4 \cdot 10$	3.9890
						0.71	0.3				
Cadmium	Cd^{106} (1.22)	1.0	Cd^{107}	6,7 hrs	e^3,	0.32	0.864	0.5			
							0.510	0.62			
							0.094	9.50	0.1		
48^{Cd}	Cd^{110} (12.4)	0.2	Cd^{111m}	49 min	IP	—	0.15	25.0		$2.2 \cdot 10^3$	5.3937
Indium	In^{113} (4.2)	56	In^{114m}	50 days	IP	—	0.772	3.5			
							0.556	3.5			
							0.192	18.5			
							1.3	0.09			
	In^{113} (4.2)	2.0	In^{114}	72 sec	β^-, e^3	~2.0	0.51	0.008			
							1.487	21.0	0.1		
49^{In}	In^{115} (95.8)	145	In^{116m}	54 min	β^-,	1.0 (51%)	1.274	75.0		$1 \cdot 10^6$	13.8155
						0.87 (28%)	1.085	54.0			
						0.6 (21%)	0.406	25.0			
	In^{115} (95.8)	52	In^{116}	13 sec	β^-	~3.0	none	—			

where $n\nu$ is the neutron flow in neutrons/cm^2/sec; σ is the cross section of the neutron activity of the elements, barns; N is the nuclear charge of the activated element; t is the irradiation time; and T is the half-life period.

It follows from the curves obtained that the indium-116 isotope has the best characteristic for its determination (activation cross section 145 b, half-life period 54 minutes). It should be noted that zinc-69 (with a half-life period 52 minutes) is the main interfering element in indium determination, but it gives a pure β-radiation which, in our setup, was completely absorbed in the aluminum filter fitted between the crystal and the sample. Analysis of the curves given in Fig. 3 gives the possibility of choosing a time interval of 5 minutes between the end of irradiation and the start of measurement. In order to standardize the apparatus, the curves

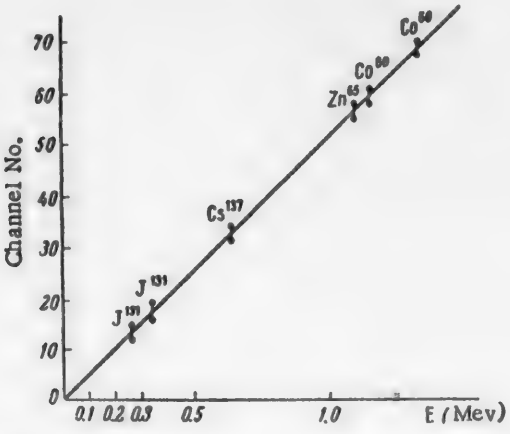

Fig. 2. The curve for the relation between the energy of the γ-quanta and the channel number.

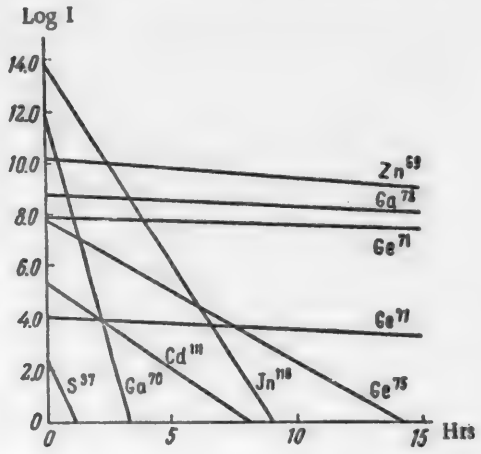

Fig. 3. Calculated curves for the drop in activity of the elements present in sphalerite.

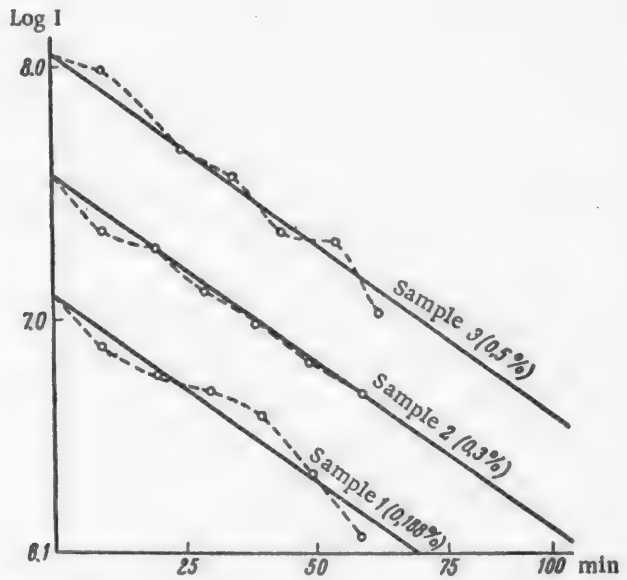

Fig. 4. Curves for drop in activity of a sample with various percentage contents of indium-116.

relating the activity of the sample and the percentage indium content of the sphalerite were constructed by means of standard samples very similar in chemical composition to natural sphalerite. Standard samples of sphalerite (ZnS) were irradiated for 3 hours 35 minutes (each) with slow neutrons from a polonium-beryllium source with an activity of 35 C. During this period it is indium-115 alone which is activated in practice.

The γ-radiation spectrum of the samples was measured by means of a scintillation γ-spectrometer. The shape of the γ-radiation spectrum of the indium-116 isotope is shown in Fig. 1, together with an indication of the energies on the photopeaks. In contrast to the data given in [5], where identification of the radioactive isotopes was carried out on the basis of the half-life periods, we investigated the change in intensity of the photopeaks (on the energy spectrum) with time; in our case the isotope was identified both by means of the characteristic lines of the spectrum (where there are no interfering lines of other isotopes), and by means of the half-life period. The decay curves were constructed on the basis of the change in the intensity of the photopeaks which allows one to avoid possible interfering radiation from other isotopes present in the sample. A similar method [6] was used first for the quantitative determination of indium in cylindrites. Before measuring the indium activity one must be sure that the activity of the sample is determined by the indium isotope, and not by some other isotope. For this purpose the activity of the indium isotope was measured in the course of two half-life periods, and the decay curves then constructed (Fig. 4). From these curves it is evident that the γ-radiation of the sample does actually correspond to the indium-116 isotope with a half-life period of 54 minutes. The points obtained on the curves were given a preliminary treatment by the method of least squares. In Table 2 are given the results obtained during measurements of the activity of samples with varying indium contents. In Fig. 5 is shown the curve relating activity to percentage indium content for a 5 minute time interval of measurement, and a sample weight of 5 g. It is clear from the curves that on increasing the percentage indium content, the activity conforms to a linear law. On the basis of Fig. 5 a nomogram was constructed for determining the percentage indium content in samples of different weight (Fig. 6). After standardizing the apparatus and constructing the nomogram, a series of measurements were made of the indium concentration of sphalerite samples taken from various deposits in the Uzbek SSR (Table 3). The deviation between these results does not

TABLE 2

Measurement of the Activity of Standard Samples

Activity N, cpm	Log N	Activity N, cpm	Log N
Sample 1 (In = 0,168%)		Sample 3 (In = 0,5%)	
1231	7.1148	1820	7.610
1010	6.917?	1566	7.460
887	6.787?	1477	7.320
838	6.7310	1154	7.180
764	6.6386	Sample 4 (In = 0,1%)	
610	6.4135	781	6.6606
489	6.1924	680	6.5221
Sample 2 (In = 0,3%)		578	6.3596
1906	7.580	521	6.2384
1591	7.3715	430	6.0638
1428	7.2993	388	5.8610
1261	7.1389	321	5.7715
1132	7.0300		
950	6.8565	Sample 5 (In = 0,05%)	
833	6.7171	495	6.2046
Sample 3 (In = 0,5%)		432	6.0685
3090	0.035	380	5.9404
2700	7.890	319	5.7653
2150	7.750	275	5.6168
		251	5.5255
		205	5.3230

exceed 7% on an average, this is fully satisfactory for low (0.02%) indium concentrations. The errors which are caused by statistical measurement do not exceed ± 3%. The error introduced into the irradiation and measurement process (because of differences in the conditions of irradiation and measurement) lies within the limits ± 2-3% (for indium contents of the order of 0.1%). The effect of statistical errors can be decreased by increasing the counting rate, i.e., by increasing the weight of sample. Thus, when the sample weight is 50 g the statistical error does not exceed 1%.

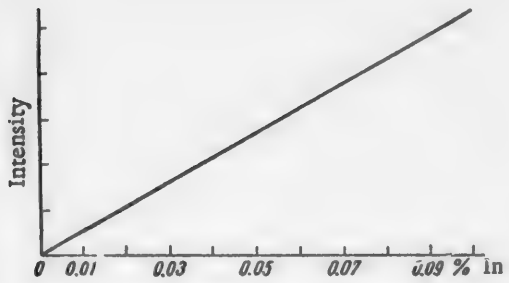

Fig. 5. Curve relating activity to percentage indium content.

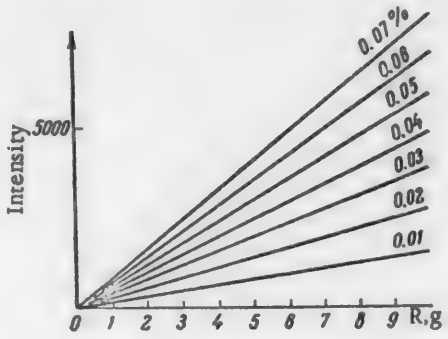

Fig. 6. Nomogram for determination of the indium content of sphalerites

What has been said shows that the given technique allows one (on increasing the neutron current) to determine fairly accurately small contents of indium in samples without radiochemical treatment of these samples.

TABLE 3

Determination of Indium by Chemical, Spectrographic, and Radioactivation Methods

Sample No.	Indium found, %		Deviation %	Sample No.	Indium found, %		Deviation %
	by chem. and spectrographic methods	by radioactivation method			by chem. and spectrographic methods	by radioactivation method	
7872	0.3	0.32	6.7	3601a	0.05	0.048	4.2
2247a	0.011	0.012	9.1	5620	0.07	0.068	10.4
281/n	0.02	0.022	10	4221	0.09	0.092	2.2
4760	0.03	0.028	7.15	3350	0.016	0.018	12.5
2724	0.02	0.021	5	5120	0.012	0.013	4.1

It should be noted that the duration for which the samples are irradiated can be decreased, and the sensitivity of the method can be increased, by increasing the power of the neutron source.

When a mark-space ratio neutron generator giving a current of 5×10^9 neutrons/4π sec is used, the duration of irradiation for the indium isotope is reduced to 10-15 minutes; when a suitable apparatus is available this should ensure an express quantitative determination of indium in rocks during core sampling by electrical means.

In conclusion, the authors wish to thank S. T. Badalov for gifts of samples for analysis.

SUMMARY

A method has been developed for the determination of the indium content of sphalerites; it is based on measurement of the γ-ray spectrum intensity of the activated samples by means of a scintillation γ-spectrometer. The concentration limits for the determination of indium in sphalerites is 0.1-0.01%. The probable experimental error is 5-10%. The method does not require radiochemical treatment of the samples.

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* Original Russian pagination. See C. B. translation.

THE USE OF THERMOGRAVIMETRY IN ANALYTICAL CHEMISTRY

COMMUNICATION 2. A THERMOGRAVIMETRIC STUDY OF PLUTONIUM COMPOUNDS*

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The thermogravimetric method has been widely used by K. Duval [1, 2]. However, the thermobalances which he used were complicated and, accordingly, several authors have developed balances of simpler design [3-6]. The thermobalance which we have made was described in detail in [6]. Recently, an air damper has replaced the additional magnetic damper. The magnetic damper used originally required special calibration because of nonlinear readings on the ends of the scale.

The air damper consists of two assemblies of aluminum cylinders arranged concentrically at a distance of 5 mm from each other. A thermogravimetric study of a number of plutonium compounds was carried out on such a thermobalance.

Papers devoted to the thermogravimetric study of plutonium compounds have appeared recently [7, 8]. One of these papers [7], however, does not give any concrete experimental data, while in the other [8], only one compound – plutonium sulfate – was studied.

In our first communication [6] the thermogravigrams shown were expressed within the coordinates: change in weight (in scale divisions) – temperature. In the work described here, all the curves are presented within the coordinates: changes in weight of an aliquot (in %) – temperature. This facilitates establishment of the composition of intermediate compounds during a thermal decomposition.

According to B. Cunningham [9] pure crystalline plutonium dioxide contains 88.19% Pu. We have determined the percentage content of plutonium in the dioxide obtained from an accurately weighed aliquot of pure plutonium metal dissolved in 6 N HCl. The hydroxide was precipitated from solution by means of ammonia free from ammonium carbonate. The hydroxide was calcined at 1050°. Taking into account the negligible loss in the filtrate, the weight of dioxide obtained corresponded to a content of 88.23% of plutonium. We used this value in our subsequent calculations.

Since, from the point of view of gravimetric analysis, the most interesting parts of a thermogravigram are those parts on which no change in weight occurs with temperature changes, i.e., the areas corresponding to stable gravimetric forms, the first step is to characterize the temperature range which corresponds to such a plateau. We are of the opinion that one can only speak of a stable compound when its weight remains constant over a range of approximately 20°. In order to confirm the existence of a plateau it is necessary to carry out a repeated thermogravimetric study of the compound prepared, in this case, however, during the time that this horizontal part of the thermogravigram is being studied (not less than one hour) the temperature should be controlled thermostatically. When, under such conditions, the weight of the residue remains constant, it can be assumed that a stable compound is formed.

* For Communication 1, see [6].

During a thermogravimetric study the temperature changes over a very wide range (20-1200°). Over this range the temperature can only be recorded by means of a Pt/Pt − Rh thermocouple, which, as is known, is calibrated with an accuracy of 1°. In our experiments the temperature was recorded visually on a pyrometer with a whole scale division of 20°. The accuracy with which the temperature was determined was about 5°.

We have studied the following plutonium compounds: the sulfate, iodate, oxalate, and 8-hydroxyquinolate.

Plutonium Sulfate. Some authors [8, 9] recommend anhydrous plutonium sulfate as a gravimetric form, since this compound has a more favorable conversion factor than plutonium dioxide, requires a low calcining temperature, and is readily dissolved after calcination. We have examined both plutonium sulfate tetrahydrate and anhydrous plutonium sulfate.

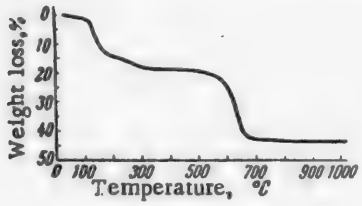

Fig. 1

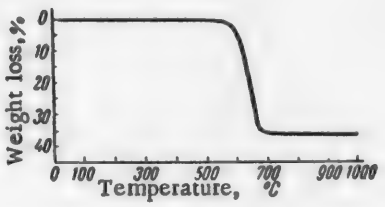

Fig. 2

The hydrated sulfate was precipitated by Anderson's method [10], by adding methanol to sulfuric acid solutions of plutonium. In Fig. 1 is shown a thermogravigram for hydrated plutonium sulfate. It is clear from this thermogravigram that all four water molecules have been lost by 270-280°. In the range 280 to 450° the curve has a plateau which corresponds to the anhydrous sulfate $Pu(SO_4)_2$. Above 450° the sulfate decomposes, decomposition is complete at 800° with formation of the dioxide.

Anhydrous plutonium sulfate was prepared by a method described by Drummond and Welch [8] (evaporation to dryness with H_2SO_4). A thermogravigram for anhydrous plutonium sulfate is shown in Fig. 2. It is clear from this that the sulfate is stable up to 500°.

Plutonium Iodate. There is no information at all in the literature [9, 11] as to the possibility of using plutonium iodate as a gravimetric form. Plutonium iodate was prepared by a technique which had been developed for precipitation of thorium iodate [12]. The precipitate obtained, after standing for two hours, was filtered off and washed with 0.05 N HNO_3 and with alcohol. The thermogravigram for plutonium iodate is shown in Fig. 3, three drops in the curve are clearly visible; the first corresponds to the removal of adsorbed water from the precipitate, this process is complete at 150°. The area on the curve covering the range 200-250° corresponds to the anhydrous iodate $Pu(IO_3)_4$.

The second drop on the curve corresponds to partial removal of oxygen with formation of an intermediate compound which is stable from 350-450°. A further increase in temperature above 450° leads to rapid decomposition of this compound to give plutonium dioxide.

Plutonium Oxalate. The oxalate of quadrivalent plutonium is one of the least soluble salts of plutonium. This oxalate is known to be precipitated with six molecules of water. There is, however, no definite information on the possibility of using this compound as a gravimetric form.

Plutonium oxalate hexahydrate was precipitated from nitric acid solutions by a method described by Cunningham [9]. In order to ensure complete precipitation, the yellow-green precipitate was allowed to stand overnight. It was washed with a 2% aqueous solution of oxalic acid and was dried under suction for one hour. The thermogravigram for the hexahydrate of plutonium oxalate is shown in Fig. 4. As is evident from this diagram, plutonium oxalate loses its six molecules of water within the range 30 to 110°. The short horizontal section on the curve at 120-150° corresponds to anhydrous plutonium oxalate. A further decrease in weight is connected with decomposition of plutonium oxalate to form plutonium dioxide. This process occurs in two stages. Initially plutonium carbonate is formed, at a temperature of 250° the carbonate starts to change into the dioxide. Accordingly, on the thermogravigram, at a temperature of 250°, we have a sharp break corresponding to this change. The sequence in which the oxalate decomposes can be represented by the following equations:

$$Pu|C_2O_4|_2 \cdot 6H_2O \rightarrow Pu|C_2O_4|_2 + 6H_2O$$
$$Pu|C_2O_4|_2 \rightarrow Pu|CO_3|_2 + 2CO$$
$$Pu|CO_3|_2 \rightarrow PuO_2 + 2CO_2$$

Plutonium 8-Hydroxyquinolate. The number of organic derivatives of plutonium used in gravimetric analysis is small [14]. Its 8-hydroxyquinolate has been used by some authors for isolating plutonium from various solutions.

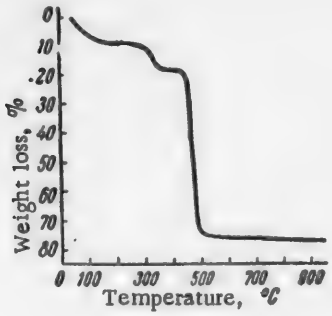

Fig. 3.

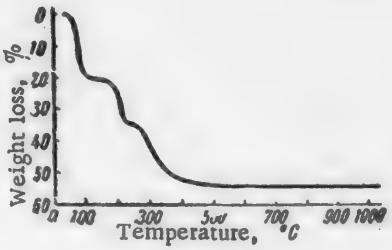

Fig. 4

The 8-hydroxyquinolate of quadrivalent plutonium was prepared as follows. To 10-15 ml of a nitric acid solution of a plutonium (IV) salt (3 mg Pu/ml and 1 N HNO_3) was added 10-15 ml of a 10% solution of ammonium tartrate, 5 ml of water saturated with SO_2, a few drops of 20% ammonia solution, and, after mixing, the solution obtained was heated to 50-70°. Next was added 20 ml of a 10% $NaHCO_3$ solution heated to 50-70°. The plutonium was precipitated by dropwise addition of a 3% solution of 8-hydroxyquinoline (excess reagent 0.5-1 mg/ml). The red-brick crystalline precipitate which separated out was kept for 2 hours on a water bath. The filtered precipitate was washed with hot wash liquor (1% with respect to $NaHCO_3$ and 0.05% with respect to 8-hydroxyquinoline) and then with hot water, a few drops of ammonia being added until the filtrate was completely clear. The precipitate was dried on the filter under suction for one hour.

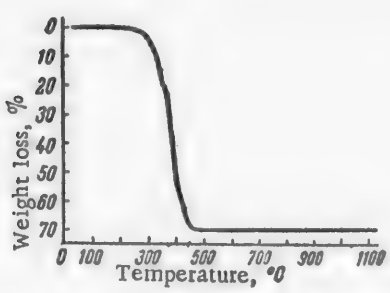

Fig. 5

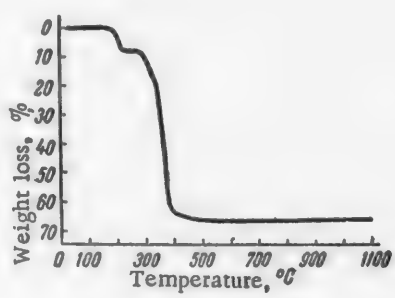

Fig. 6

In Fig. 5 is shown the curve illustrating the thermal decomposition of plutonium-8-hydroxyquinolate. Analysis of this curve shows that the 8-hydroxyquinolate is stable up to 220° and that it has the formula $Pu(C_9H_6NO)_4$. Decomposition of this compound occurs at 300-500° with formation of plutonium dioxide. When the precipitate has not been washed free enough from precipitant, the thermogravigram (Fig. 6), at a temperature of about 200° shows an additional drop corresponding to removal of excess 8-hydroxyquinoline. Calculation shows that the small plateau on the thermogravimetric curve at 250° corresponds to the normal 8-hydroxyquinolate $Pu(C_9H_6NO)_4$. Although 8-hydroxyquinoline itself starts to sublime at 85° [13], removal of excess of the reagent from the precipitate proceeds at a considerably higher temperature (about 200°), this indicates that there is a link between the molecule of precipitant and the precipitate of plutonium 8-hydroxyquinolate.

DISCUSSION OF RESULTS

Of the compounds which we have examined the ones which have the most favorable conversion factors are the iodate and 8-hydroxyquinolate of plutonium (Table 1). These compounds do not require a high calcining temperature.

TABLE 1

Precipitant	Gravimetric form	Conversion factor to Pu	Temp. range over which gravimetric form is stable, °C
Sulfuric acid + + methanol	$Pu(SO_4)_2$	0.554	280—450
	PuO_2	0.882	>800
Sulfuric acid	$Pu(SO_4)_2$	0.554	20—500
	PuO_2	0.882	>800
Potassium iodate	$Pu(JO_3)_4$	0.254	200—250
	PuO_2	0.882	> 800
Oxalic acid	$Pu(C_2O_4)_2$	0.576	120—150
	PuO_2	0.882	>600
8-Hydroxyquinoline	$Pu(C_9H_6NO)_4$	0.293	50—230
	PaO_2	0.882	>700

Plutonium sulfate — a compound with a fairly favorable conversion factor (0.554) and a large temperature range over which it is stable — is little used in gravimetric analysis. Plutonium sulfate recommends itself as a gravimetric form because the residue of plutonium sulfate obtained after calcining up to 450° is readily brought into solution.

Decomposition of plutonium compounds to give the dioxide finishes at higher temperatures in those cases where it is formed from inorganic compounds than in cases where it is formed from organic compounds.

The results obtained make it possible to establish more favorable temperatures for drying and calcining the compounds studied.

We have carried out special experiments to confirm the formation of compounds of a definite composition within the given temperature ranges. After calcination, the percentage plutonium content of the compounds isolated was determined by means of an α-count. The results obtained are given in Table 2.

TABLE 2

Formula	Pu content, %		Calcining temp. °C
	calc.	found	
$Pu(SO_4)_2$	55.45	55.70—55.31	450
$Pu(JO_3)_4$	25.45	25.30—25.26	200
$Pu(C_2O_4)_26H_2O$	45.69	45.50	20
$Pu(C_2O_4)_2$	57.59	57.10	140
$Pu(C_9H_6NO)_4$	29.3	28.71—29.46	230

As is evident from the results given in this table, we obtained values close to the theoretical values.

SUMMARY

It has been shown that $Pu(SO_4)_2$ obtained from both plutonium sulfate tetrahydrate and the anhydrous sulfate can be used as a gravimetric form.

When plutonium iodate is used in gravimetric analysis, it is essential to wash it free from excess precipitant, the precipitate can then be dried at 200°.

It has been shown that the anhydrous oxalate of quadrivalent plutonium can be used for gravimetric determinations. For this purpose, plutonium oxalate hexahydrate should be dried at 140-150°.

Plutonium 8-hydroxyquinolate, after drying at 230° (not above 250°) corresponds to the formula $Pu(C_9H_6NO)_4$ and can be used as a gravimetric form.

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QUANTITATIVE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN THE RARE EARTHS

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The sensitivity of x-ray spectrographic determination of impurities in the rare earths, which is equal to 0.1%, is already insufficient for controlling modern production of preparations of the rare earths.

Encouraging results are given by emission spectrographic methods of analysis, such methods enable one, with small expenditure of test material, to attain a high sensitivity which amounts to 0.02-0.005% for yttrium group elements.

Improvement in methods of emission spectrographic determination of the rare earths has taken place very slowly [1-24], as a consequence of the complexity of their spectra and the nonavailability of spectrographically pure preparations which are essential for identification of lines and for preparation of standards.

The most important and most systematic work along this direction has been carried out by Fassel and coworkers [5, 11, 12, 16, 17].

Fassel's method is based on complete ignition of the sample, which is in the form of a mixture of the test element and carbon powder, the main element of the sample being suggested as the internal standard. In order to carry out an analysis by Fassel's method about 15 mg of sample is necessary. Developing the work of Fassel, Grishina recently [18, 19] suggested a method for the determination of a number of impurities in pure preparations of the rare earths, in which solutions of the chlorides placed on the face of a carbon or copper electrode are used. The method is characterized by high sensitivity (0.02-0.05%) and only uses up a very small amount of material (2-4 mg). The experimental error is 5-10%.

The problem which we set ourselves was to determine the range of elements which may be present as impurities in various preparations during their purification. For this purpose, we subjected to qualitative, and, subsequently, to semiquantitative spectrographic analysis, a number of rare earth preparations, the impurity content of which was less than the sensitivity of determination by x-ray spectrographic methods.

The distribution of impurity elements in various rare earth preparations, after their purification by chromatographic methods, is shown in Table 1.

As is evident from the table, the purified rare earth preparations contain as impurities mainly the neighboring elements in the periodic system. Development of methods for the determination of these neighboring elements should take precedence.

We have developed the following analytical method for the quantitative determination of small amounts of impurities, this method does not require the use of pure preparations for preparing standards. In essence, the method depends on using the relationship between the line intensity and the absolute content of the test element in the sample being analyzed. One standard, which is one of the samples carefully analyzed by an x-ray spectrographic method, is used for carrying out an analysis.

The content of rare earth impurities in this sample should be higher than the sensitivity limit of the x-ray spectrographic methods of analysis (> 0.1%) and should lie within the range 0.5-1%.

TABLE 1

Distribution of Impurity Elements in Some Rare Earth Preparations

Test element	Impurity element content, %
Pr	Eu ~ 0.01
Nd	Pr ~ 0.1
Sm	Eu ~ 0.1
Eu	Sm ~ 0.5; Gd ~ 0.02
Gd	Tb ~ 0.02
Tb	Dy ~ 0.02; Gd ~ 0.04; Y ~ 0.01
Y	Yb ~ 0.007; Ho ~ 0.02; Dy ~ 0.04; Tb ~ 0.04; Gd ~ 0,02
Dy	Y ~ 0.04; Ho ~ 0.03; Tb ~ 0.02
Ho	Dy ~ 0.02
Er	Yb ~ 0.006
Tu	Yb ~ 0.006
Lu	Yb ~ 0.02; Tu ~ 0.02

In order to determine impurities, the content of which is less than 0.1%, a curve showing the relation log I = f (log m) – where I is the line intensity, m is the absolute content of the element, and is proportional to the weight of sample taken – is constructed on the basis of this standard. By decreasing the amount of sample, it is possible to follow the path of the calibration curve right down to very low values of the absolute content, which are limited by the absolute sensitivity of the spectrographic determination of the elements. In order to establish the path of the calibration curve more reliably in regions of low m and high m, several standards* are used.

Fig. 1. Radiograph of the distribution of La-140 in the body of a carbon electrode after placing ten drops of a 5% solution of the La-140 isotope in 1% hydrochloric acid on its face. On the right: without treatment of the electrode face with polystyrene; on the left: the electrode was treated with polystyrene before putting the lanthanum isotope on it.

Bearing in mind the necessity for cutting down the amount of material expended, we used a solution of the chlorides of the rare earths in order to develop the method, the solutions being placed on the face of the electrode, since under such conditions, the amount of material expended is a minimum.

Standards and test samples are dissolved as follows.

Rare earth oxides are dissolved in concentrated hydrochloric acid on heating. The solutions are evaporated to dryness, and from the chlorides obtained, 5% solutions of the rare earths in 1% hydrochloric acid are prepared. One drop of this solution is placed on the face of a carbon or copper electrode, the latter being then dried on a hot plate. 5%, 3%, 1%, 0.3%, etc. solutions of the main standard are used as standards.

In the spectral regions 3100-3500 A, 4200-4600 A carbon electrodes are used, while in the region 3750-4200 A copper electrodes are used. An ac arc is used for spectra excitation.

A special study was made of the treatment of the electrodes prior to placing samples on them. For this purpose, radioactive preparations of the rare earths were placed on the faces of the electrodes, the electrodes were then examined radiographically. It was established that the rare earths are distributed fairly evenly on the electrode face, but diffusion into the body of the electrode occurs (Fig. 1), and this leads to some drop in sensitivity. In order to eliminate this diffusion, the carbon electrode was covered beforehand with a polystyrene

* Naturally, in the m region the analytical lines should be free from self-absorption.

film, the latter being formed by drying out a 3% solution of polystyrene in benzene on the face. This polystyrene treatment ensures that the rare earths are concentrated on the electrode surface only (Fig. 1).

The spectra were taken by means of a Baird Associates diffraction spectrograph which had a dispersion of 5.5 A/mm in the first order. Two electrodes plus samples were exposed on the same place on the photographic plate. The analytical conditions are given below.

Spectrograph	Baird Associates with a diffraction grating, second order, dispersion 2.75 A/mm.
Slit width	25 μ.
Illumination	Single lens system.
Electrodes	Copper or carbon with a diameter of 6 mm. The upper electrode was sharpened to a cone.
Excitation source	ac arc generator.
Current	10 a for carbon electrodes and 8 a for copper electrodes.
Exposure	60 sec. Two electrodes plus samples were exposed on the same place for 30 sec. each.
Plates	Spectrographic, type II, sensitivity 16 or 22 GOST units.
Developer	Meto-hydroquinone
Calibration of emulsion	Sector or stepwise attenuator

TABLE 2

Analytical Lines for the Determination of Impurities in the Rare Earths

Impurity	Base	Wavelength of the lines, A: analytical lines	Wavelength of the lines, A: reference line for analysis by three standards method	Conc. range, %	Electrodes
La	Pr	3337.49	3337.19	0.005—0.2	Carbon
Sm	Nd	4433.88	4436.68	0.05 —0.2	"
Eu	Nd	4435.53	4436.68	0.01 —0.1	"
Pr	Nd	4408.84	4419.62	0.1 —1.0	"
Sm	Eu	4424.34	4357.04	0.05 —1.0	"
Yb	Eu	3289.85	3288.57	0.008—0.5	"
Eu	Gd	4435.53	4437.45	0.02 —0.2	"
Tb	Gd	3324.40	3321.7	0.01 —0.2	"
Dy	Tb	3898.54	3893.73	0.02 —0.2	"
Gd	Tb	3350.48	3347.8	0.02 —0.2	"
Gd	Tb	3768.41	3761.9	0.02 —0.2	Copper
Y	Tb	3982.59	3986.97	0.02 —0.2	Carbon
Y	Tb	3774.33	3761.9	0.02 —0.2	Copper
Y	Dy	3774.33	3777.9	0.003—0.2	"
Er	Ho	3906.32	3910.3	0.02 —0.1	"
Dy	Ho	4211.72	4219.2	0.02 —0.2	"
Ho	Er	4103.84	4104.02	0.02 —0.2	"
Tu	Er	3362.61	3369.23	0.008—0.2	Carbon
Tu	Yb	3362.61	—	0.003—0.2	"
Dy	Y	3407.80	3469.43	0.01 —0.2	"
Tb	Y	3218.93	3182.42	0.02 —0.2	"
Yb	Tu	3289.37	3291.00	0.008—0.2	"
Yb	Lu	3289.37	3171.36	0.003—0.2	"
Tu	Lu	3362.61	—	0.008—0.2	"

Table 2 contains the recommended analytical lines. These lines were chosen on the basis of the spectra of decreasing amounts of samples. Identification and checking of the lines for absence of superposition was carried out by controlling the change in the line intensity during the purification of the preparations.

In order to decipher and distinguish spectra of different orders we used a color photography method suggested earlier [20]; this is based on the fact that lines of different orders have different colors. This makes it possible to remove foreign lines readily by means of their color, and to isolate false "ghost" lines.

Calibration curves are constructed within the coordinates log I, log m; in the region of normal blackening, within the coordinates S, log m; where $\underline{m}$ is the absolute content of the elements determined. In Fig. 2, as an example, is shown one of the calibration curves obtained.

The mean square error for a single determination by the method indicated is 25-30%.

Bearing in mind the close physicochemical properties of the rare earths, one might expect that the calibration curves constructed for the determination of impurities in some rare earth preparation might coincide with the calibration curves* for the determination of the same impurities in other rare earth preparations.

Experiments, which we carried out on materials based on erbium and yttrium, showed that, in actual fact, coincidence of the calibration curves does occur for the elements indicated (Fig. 3). It can be assumed that coincidence of calibration curves will also take place for other rare earths.

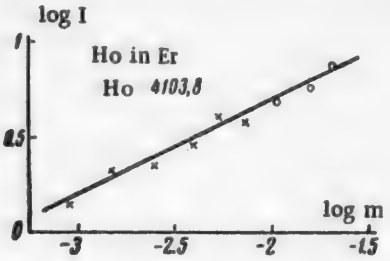

Fig. 2. Calibration curve for the determination of holmium in erbium by the method of diluting the standard. ○) Basic standards analyzed by x-ray spectrographic analysis; x) standards obtained by diluting the basic standard.

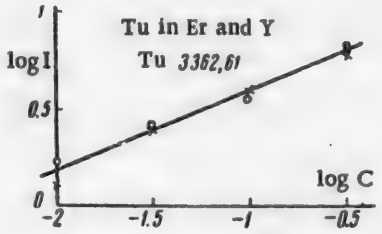

Fig. 3. Calibration curve for the determination of thullium in erbium and yttrium. ○) Points belonging to erbium; x) points belonging to yttrium.

In order to check on the absence of systematic errors during determinations by the methods described above, we also used the three standards method.

Standards were prepared by the usual methods from the purified preparations. Calibration curves were constructed within the coordinates ΔS, log C or $\log \frac{I_{line}}{I_{mean}}$, log C. The recommended analytical lines and the reference lines used in this method are also given in Table 2. The analytical conditions were the same as those described above.

TABLE 3

Comparison of the Results Obtained During the Determination of Thullium and Holmium in Erbium by Various Methods

Introduced, %	Found by the method of diluting a standard, %	Found graphically on a yttrium base, %	Found graphically on an erbium base, %
Tu in Er 0.03	0.02	0.035	0.033
Error	33%	16.7%	10%
Ho in Er 0.04	0.03	0.045	0.043
Error	25%	12.5%	7.5%

* Within the coordinates S, log C or log I, log C.

The mean square error of a single determination by the three standards method is 10-15%.

Table 3 contains results obtained during the determination of Tu and Ho in Er.

As is evident from the table, the analytical results coincide within the limits of experimental error.

The authors wish to thank E. E. Vainshtein for his help and valuable advice during the course of this work.

SUMMARY

A method has been developed for the quantitative spectrographic determination of small amounts of impurities of La in Pr; Sm, Pr, and Eu in Nd; Sm and Yb in Eu; Eu and Tb in Gd; Y, Dy, and Gd in Tb; Y in Dy; Er and Dy in Ho; Ho and Tu in Er; Tu in Yb; Dy in Y; Tb in Y; Yb and Tu in Lu; and Yb in Tu.

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A CHEMICOSPECTROGRAPHIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM AND TUNGSTEN IN THE PRESENCE OF LARGE AMOUNTS OF IRON

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Spectrographic determination of small amounts of molybdenum and tungsten in ores and meteorites containing more than 15% of iron is connected with considerably difficulties, and, in the presence of more than 90% of iron, such a determination becomes impossible. In order to carry out an analysis under these conditions it is necessary to separate the test elements quantitatively from iron beforehand. In the work described here we used ion exchange chromatography for this purpose.

Ion exchange chromatography has been used for separating molybdenum from other metals, including iron [1-6]. Chromatographic separation of tungsten has been studied in less detail, while the possibility of using this method for the simultaneous separation of Mo and W from rocks, has not been examined hitherto, as far as we know.

One of the methods for separating Mo and Fe is based on making use of the property of molybdenum to form a peracid with H_2O_2, this compound is not held back on a cation exchange resin and passes through into the filtrate, while iron is held on the resin [1]. The possibility of separating molybdenum from accompanying elements in the form of its citrate complex has been noted [2, 6]. In order to choose the optimum conditions for carrying out chromatographic experiments and to establish the possibility of simultaneously separating the elements from rocks, the radioactive isotopes Mo^{99} and W^{185} were used.

Experiments were carried out on a column 10-12 mm in diameter containing 10-12 g of the cation exchange resin KU-2. The solution was passed through the column at the rate of 2-3 ml/min. The optimum acidity and the volume of wash liquors, and the H_2O_2 concentration or that of the complexing agent used for separating Mo and W from iron, were established using solutions containing 120 mg of Fe in the form of ferric alum, and 0.1 mg of Mo or W in the form of ammonium molybdate or tungstate. The latter contained the radioactive isotopes, the radiation intensity of these isotopes in the filtrate was recorded on the basis of their β-activity by means of a torsion counter. The acidity of the solution was altered by addition of the calculated amount of sulfuric acid. The curves (Figs. 1-4) illustrate the relation between the percentage yield of Mo and W in the filtrate and the acidity of the solution and the H_2O_2 concentration in the first of the methods tested, and acidity and citric acid concentration in the second of the methods tested.

Alternate portions of filtrate were chosen and analyzed every 3 minutes. The wash solution was prepared by dissolving four drops of concentrated sulfuric acid in 100 ml of water. The minimum amount of wash liquor required for complete elution of Mo and W from the columns proved to be 150-180 ml.

Examination of the curves (Figs. 1-4) shows that the method suggested by Alimarin and Medvedeva [1] for the chromatographic separation of molybdenum from iron can also be successfully used for the quantitative

simultaneous separation of tungsten. The optimum conditions for this purpose are obtained at a H_2O_2 concentration of 1% and an acidity of 0.5 N with respect to H_2SO_4. As special checks using labelled atoms showed, under the conditions indicated, Mo and W are not held by the cation exchange resin, and pass almost completely into the filtrate. During separation of these elements in the form of their citrate complexes (Figs. 3 and 4) we were unable to obtain complete separation of tungsten, only about 75% of the original amount of this element originally present in the rock passed into the filtrate.

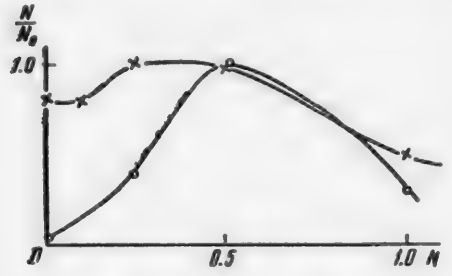

Fig. 1. The relation between the yield of W (○) and Mo (x) in the filtrate and the acidity of the solution during their chromatographic separation from iron by method [1]; the amount of labelled Mo or W atoms as a percentage of the total amount isolated is plotted on the ordinate, while the acidity expressed in g-eq H_2SO_4/liter is plotted along the abscissa.

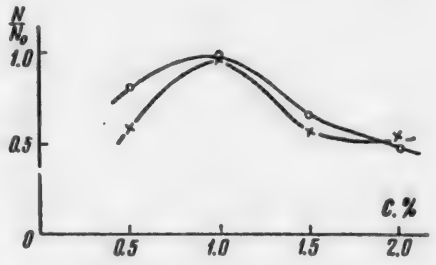

Fig. 2. Relation between sorption of W (○) and Mo (x) by the cation exchange resin and the H_2O_2 concentration expressed as a percentage.

Experimental Procedure. Having established the possibility of separating Mo and W quantitatively by a chromatographic method, from large amounts of iron, which interfere with their determination, we were able to develop a combined chemicospectrographic method for the determination of these elements in rocks, and we have successfully used this method for the analysis of meteorites. For this purpose 0.12 g of test material is heated with 15 ml of HCl (1:1), 0.5 ml of concentrated HNO_3 is added and the mixture heated again until the material has dissolved completely; the solution is then evaporated until its volume is 3-5 ml and 10-15 ml of 6 N H_2SO_4 is added, the solution is evaporated until thick fumes of SO_3 cease to be evolved. To the dry residue is added 30 ml of water and the whole heated until

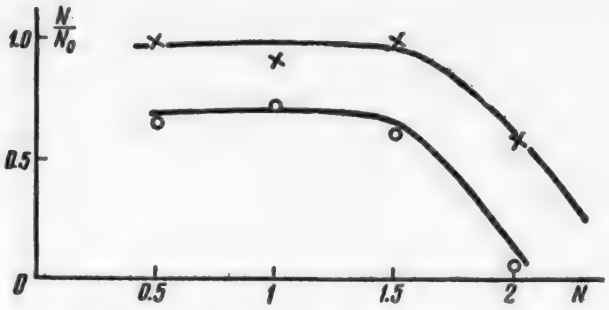

Fig. 3. The relation between yield of W (○) and Mo (x) in the filtrate, and the acidity of the solution, during their chromatographic separation from iron by method [2, 6].

complete solution is obtained. The solution is cooled and sulfuric acid added until the concentration of the solution is 0.45 N with respect to H_2SO_4 (this corresponds to a pH of 0.65), H_2O_2 is added until its concentration in the solution is 1%. The solution thus prepared is passed through a column containing KU-2 at the rate of 3 ml/min, the column is washed with 180 ml of wash liquor and all the filtrate collected and evaporated to dryness. The residue obtained is calcined to constant weight (about 2 mg); it is then diluted to 20 mg with

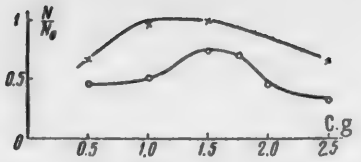

Fig. 4. Relation between yield of W (○) and Mo (×) in the filtrate and citric acid concentration expressed in g.

a silicate base which has been shown to be free from Mo and W, the mixture is divided into two portions in which Mo and W are determined spectrographically [7-9].

The reproducibility of the experimental results is ± 12 % for Mo and ± 15 % for W. The sensitivity of the chemicospectrographic method (taking into account the five-fold enrichment of the elements which occurs in our experiments during chemical preparation of the sample) is $2 \cdot 10^{-5}$ % for molybdenum and $6 \cdot 10^{-4}$ % for tungsten. This is quite satisfactory for the determination of the content of these elements in iron meteorites.

Some of the results which we obtained during such determinations are given in the table. Comparison of these results with published results [10, 11] indicates that there is good agreement between the experimental results which we obtained on using the method described and those obtained by other workers using a spectrophotometric method.

Mo and W Contents of Some Meteorites

Metallic phase of the iron meteorite	Found, % Mo	W
Meteorite "Sikhote-Alinskii"	$1.68 \cdot 10^{-3}$	$9.5 \cdot 10^{-4}$
Meteorite "Toluka"	$1.5 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$
Meteorite "Saratov"	$8.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$
Meteorite "Kunashak"	$8 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$

The author wishes to express his thanks to E. E. Vainshtein for his valuable advice, and to L. V. Meshcheryakova for help in carrying out the analyses.

SUMMARY

During the spectrographic determination of Mo and W in meteorites containing large amounts of iron, these elements are separated from the iron chromatographically.

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THE USE OF CINNAMIC ACID IN ANALYTICAL CHEMISTRY

COMMUNICATION 1. SEPARATION OF IRON, ALUMINUM, AND CHROMIUM FROM MANGANESE, NICKEL, COBALT, AND ZINC

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Methods of separating trivalent metals from divalent metals in the form of basic acetates, succinates, or formates have not found wide application. Somewhat better results have been obtained by using ammonium benzoate [1], which precipitates the basic benzoates of trivalent and quadrivalent metals at a definite pH of the solution. The basic benzoates of iron, aluminum, and chromium, however, which do not possess a constant composition and separate out in a strongly hydrated form, are capable, after they have separated out, of partially coprecipitating the divalent metals remaining in the solution (Mn, Ni, Co, and Zn), the extent of coprecipitation being dependent on the excess of precipitant added.

In order to improve the method of separating the metals indicated by hydrolysis, we decided to examine the possibility of using other acids of the aromatic series for this purpose, in the first instance we tried cinnamic acid (phenyl acrylic acid). During separation of the metals, cinnamic acid has been used for: precipitating vanadium [2]; for separating thorium from the rare earths [3]; and for precipitating zirconium [4]; for separating thorium from uranium [5]; and for separating thorium from the rare earths and from other metals [6].

Solutions of the metal chlorides were prepared for the study; the solutions were standardized gravimetrically. Our experiments showed that, under certain conditions, ammonium cinnamate quantitatively precipitates iron, aluminum, and chromium in the form of their basic cinnamates from a weakly acid solution heated to the boiling point; under these conditions, manganese, nickel, cobalt, and zinc remain in solution. During these experiments the pH of the solution was kept at 5.0-5.1.

The pH value at which separation of the basic cinnamates of the indicated metals starts, almost coincides with the pH values at which their hydroxides separate from solution.

In order to establish their composition, the precipitates were filtered off through glass filters, washed 2-3 times with water containing ammonium cinnamate, and then with alcohol. After drying to constant weight at 110°, the precipitates were analyzed. We established that iron gives a mixture of basic salts $C_6H_5CH:CH\cdot COO\cdot Fe(OH)_2$ and $(C_6H_5CH:CH\cdot COO)_2Fe(OH)$ (in the proportion of about 1:1); aluminum and chromium gives basic salts $(C_6H_5CH:CH\cdot COO)_2Al(OH)$ and $(C_6H_5CH:CH\cdot COO)_2Cr(OH)$. On using double the amount of reagent for carrying out the precipitation, the composition of the basic salts of aluminum and chromium did not change; iron, however, gave a mixture of the medium and basic salts: $(C_6H_5CH:CH\cdot COO)_3Fe$ and $(C_6H_5CH:CH\cdot COO)_2Fe(OH)$ (in the proportion of about 1:1).

In order to study the quantitative separation of iron, aluminum, and chromium, precipitation experiments were carried out under the conditions described below. The experimental results are given in Table 1. The filtrates obtained after removal of iron, aluminum, and chromium were evaporated and tested for the presence of the metals indicated; they were not detected in a single case. Precipitation in the presence of $(NH_4)_2SO_4$ and NH_4NO_3 taken in amounts of 10 g also proceeded quantitatively. The precipitates of the basic cinnamates of iron, aluminum, and chromium coagulated readily and were easily filtered and washed.

TABLE 1

Oxide	Taken g	Found g	Error g	Oxide	Taken g	Found g	Error g
Fe_2O_3	0.0550	0.0549	−0.0001	Al_2O_3	0.0005	0.0005	±0.0000
Fe_2O_3	0.0006	0.0006	±0.0000	Cr_2O_3	0.0532	0.0532	±0.0000
Al_2O_3	0.512	0.0511	−0.0001	Cr_2O_3	0.0005	0.0006	+0.0001

Experiments which were carried out in order to study the extent to which the basic cinnamates of iron, aluminum, and chromium are contaminated by the divalent metals (Mn, Ni, Co, and Zn) were carried out under the same conditions. In order to determine the divalent metals entrained by the precipitates of the trivalent metals, the precipitates were ashed and then dissolved, and Mn, Ni, Co, and Zn were determined colorimetrically in the solutions. The extent of contamination is shown in Table 2. The experimental results show that separation is fairly complete, and that there is no need to carry out a reprecipitation.

TABLE 2

Taken, g				Found in the precipitate, g	
Fe_2O_3	0.0500	MnO	0.0050	MnO	<0.00001
	0.0050	MnO	0.0500	MnO	0.00008
	0.0500	NiO	0.0050	NiO	<0.00001
	0.0050	NiO	0.0500	NiO	0.00002
	0.0500	CoO	0.0050	CoO	0.00003
	0.0050	CoO	0.0500	CoO	0.00008
	0.0500	ZnO	0.0050	ZnO	0.00006
	0.0050	ZnO	0.0500	ZnO	0.00002
Al_2O_3	0.0500	MnO	0.0050	MnO	0.00001
	0.0050	MnO	0.0500	MnO	0.00002
	0.0500	NiO	0.0050	NiO	0.00007
	0.0050	NiO	0.0500	NiO	0.00006
	0.0500	CoO	0.0050	CoO	0.00007*
	0.0050	CoO	0.0500	CoO	0.00005*
	0.0500	ZnO	0.0050	ZnO	0.00006
	0.0050	ZnO	0.0500	ZnO	0.00003
Cr_2O_3	0.0500	MnO	0.0050	MnO	0.00003*
	0.0050	MnO	0.0500	MnO	0.00004*
	0.0500	NiO	0.0050	NiO	0.00003*
	0.0050	NiO	0.0500	NiO	0.00007
	0.0500	CoO	0.0050	CoO	0.00002*
	0.0050	CoO	0.0500	CoO	0.00008*
	0.0500	ZnO	0.0050	ZnO	0.00003*
	0.0050	ZnO	0.0500	ZnO	0.00005*

* Precipitation carried out in the presence of 15 g NH_4Cl.

During separation of total trivalent metals from the divalent metals the extent of separation was also fully satisfactory.

After removal of iron, aluminum, and chromium in the form of their basic cinnamates, the divalent metals indicated were quantitatively precipitated from the filtrates by heating the latter with ammonium sulfide. Hydrogen sulfide quantitatively precipitates zinc, cobalt, and nickel, the precipitates of the last two metals separating out as crystalline sulfides, while zinc separates out in the form of an amorphous, fairly dense sulfide. Under these conditions, manganese does not separate out at all initially, only after some time does a slight turbidity appear. During separate determination of the divalent metals in the filtrates, manganese was precipitated in the form of manganese ammonium phosphate which was then calcined to the pyrophosphate. Nickel was isolated, as usual, by means of dimethylglyoxime from a weakly ammoniacal medium, and was left to stand overnight. Cobalt was isolated by means of α-nitroso-β-naphthol from a heated solution acidified with hydrochloric acid. The precipitate was carefully ashed to the oxide which was dissolved in HCl, after

evaporating and neutralizing this solution, the cobalt was isolated as its anthranilate [7]. Zinc was isolated by means of an alcoholic solution of hydroxyquinoline from a heated, weakly ammoniacal solution, and, after the precipitate had been washed, it was calcined to zinc oxide. Completely satisfactory results were obtained (Table 3).

TABLE 3

Taken, g		Found, g	Error, g
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	MnO 0.0107	MnO 0.0109	+0.0002
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	NiO 0.0107	NiO 0.0107	±0.0000
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	CoO 0.0104	CoO 0.0105	+0.0001
Fe_2O_3 0.0100 Al_2O_3 0.0100 Cr_2O_3 0.0100	ZnO 0.0104	ZnO 0.0105	+0.0001

Preparation of the Reagent. A solution of ammonium cinnamate (5% with respect to cinnamic acid) is used as the reagent. 25 g of pure cinnamic acid is placed in a 750-800 ml conical flask (having a mark at 500 ml) fitted with a glass stopper. Approximately 80 ml of water is added and the contents of the flask mixed to a homogeneous paste with a glass rod with a widened end, care being taken to break down any lumps. A further 200 ml of water is added and a 10-12% solution of distilled ammonia added in small portions with vigorous stirring, until the cinnamic acid has almost completely dissolved (a small amount of material should be left, while the liquid should not smell of ammonia). A small amount (about 1.5 g) of cinnamic acid is added and the whole thoroughly mixed after stoppering the flask. The solution should give a weak acid reaction to litmus. Water is added to bring the volume up to 500 ml and the whole thoroughly mixed again; the final solution is left to stand overnight and then filtered through a "blue band" filter. The reagent is stored in dark colored glass bottles fitted with glass stoppers. The reagent is stable, a small amount of a crystalline sediment of cinnamic acid separates out with time, but this does not interfere.

Experimental procedure. It is best to have a hydrochloric acid solution which does not contain more than 0.1 g of the sesquioxides (sulfates and nitrates do not interfere).

To about 60 ml of the acid solution is added 10 g of ammonium chloride. In those cases when the trivalent metals present are mainly aluminum or chromium, and the iron content is very low, the amount of NH_4Cl should be increased to 15 g. The solution is carefully neutralized with dilute ammonia, the latter being added dropwise with stirring until a faint turbidity appears, the latter is destroyed by addition of 2-3 drops of hydrochloric acid sp. gr. 1.12. When large amounts of iron are present, neutralization is carried out to the appearance of a brownish color, the latter too being destroyed by addition of the indicated amount of hydrochloric acid. The solution obtained is diluted with water to approximately 80-90 ml and then heated to the boil. Having adjusted the flame so as to maintain gentle boiling, 20 ml of the reagent is added dropwise from a dropping funnel with a bent tip, the solution being vigorously stirred at the same time with a glass rod.

On completion of the precipitation, the beaker is covered with a clock glass and the liquid allowed to boil weakly for 1-2 minutes (in the presence of large amounts of chromium, up to 3 minutes). The beaker is then transferred to a water bath for 1-1.5 hours. The liquid is stirred from time to time while it is on the water bath. After the precipitate has settled out, the liquid is filtered through a "white band" filter, during this stage the liquid is carefully decanted, while endeavouring not to disturb the mass of the precipitate. The precipitate remaining in the beaker is washed twice by decantation with hot wash liquor (10 g of NH_4Cl is dissolved in hot water, 20 ml of reagent is added, and the volume made up to 100 ml), using 20-25 lots of the latter. The precipitate is finally transferred onto the filter and washed with hot wash liquor (to 20 ml of reagent is added

280 ml of hot water). The washed precipitate is transferred to a crucible, in which it is carefully dried and ashed.

Manganese, nickel, cobalt, and zinc can be separated from the filtrate by means of ammonium sulfide on heating. Subsequently, zinc can be removed in the form of its sulfide [8], nickel and cobalt are separated from manganese by precipitating them in the form of their crystalline sulfides by means of hydrogen sulfide in the presence of a buffer mixture consisting of pyridine and its hydrochloride [9]. When only one of the divalent metals is present, it can be isolated and determined as indicated earlier.

The method can be used for the analysis of the most diverse materials such as manganese ores and concentrates, marine iron-manganese concretions, nickel, cobalt, and zinc ores, and various alloys.

SUMMARY

It has been established that ammonium cinnamate quantitatively precipitates iron, aluminum, and chromium in the form of their basic salt from a weakly acid solution on heating; under the same conditions, manganese, nickel, cobalt, and zinc remain in solution.

The basic cinnamates of iron, aluminum, and chromium are precipitated in a dense form which is readily filtered and washed. Sorption of the divalent metals (Mn, Ni, Co, and Zn) by the precipitates of the basic salts is so negligible, that separation can be effected after only one separation. Sulfate and nitrate ions do not interfere.

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A METHOD FOR THE INDIRECT POLAROGRAPHIC DETERMINATION OF SULFATE, AND ITS USE IN WATER ANALYSIS*

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In a paper published earlier [1] a study was made of the system $SO_4^{2-} - Pb^{2+}/PbSO_4$ for the purpose of developing a method for the indirect polarographic determination of sulfate. When a solution containing sulfate, and with a definite ionic strength and temperature, is shaken with lead sulfate, a state of equilibrium is established which can be characterized by the polarographic determination of the concentration of lead ions which pass into solution. A method of determining sulfate in water is based on this principle [2].

In the present article a description is given of another method for the indirect polarographic determination of sulfate, which is based on precipitation of sulfate ions from an aqueous-alcoholic medium by addition of lead nitrate, and polarographic determination of the lead ions remaining in solution. The presence of ethanol ensures more complete precipitation of lead sulfate. Since excess lead ions are determined in the final solution polarographically, precipitation is carried out in the presence of potassium nitrate which subsequently serves as the supporting electrolyte. The new method is simpler.

Apparatus. 1) A Leybold polarograph with a capillary from the same firm; 2) a Heyrovsky polarographic cell (the temperature is controlled within the limits of ± 0.5°); 3) an ion exchange column prepared according to Tompkins et al. [3].

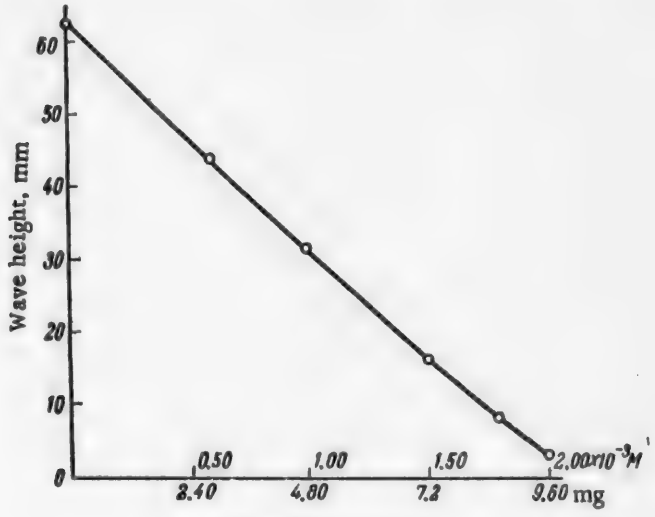
Reagents. 1) Potassium sulfate solution 0.01 M. More dilute solutions were prepared from this solution; 2) potassium nitrate solutions 0.5 and 0.1 M; 3) ethanol; 4) gelatin solutions, 0.2 and 0.4%; 5) lead nitrate solutions, 0.01 and 0.004 M; 6) Amberlite IR-120 (in the H-form).

Preliminary Experiments. In order to establish the optimum conditions for the indirect polarographic determination of the concentration of lead ions in solution (in the absence of sulfate) a solution with a concentration of 10^{-3} M was taken, this concentration is the optimum for measuring the diffusion current of lead ions. The solubility of lead sulfate drops strongly in a medium containing 25% ethanol; higher ethanol concentrations lead to coprecipitation and decrease the height of the polarographic wave of the lead ions. As for the concentration of the supporting electrolyte, we obtained satisfactory results on using 0.025 M solutions of potassium nitrate. At higher supporting electrolyte concentrations, low and poorly reproducible results were obtained during the indirect polarographic determination of sulfate on account of partial precipitation of the latter as the double salt $PbSO_4 \cdot K_2SO_4$, as has been demonstrated by Kolthoff and Pan [4].

A calibration curve which was constructed as described below is shown in the figure: 50 ml lots of potassium sulfate solution with concentrations of O (water), 0.60, 1.00, 1.50, 1.80, and $2.00 \cdot 10^{-3}$ M were placed in 250 conical flasks. To these solutions were added 5.0 ml of 0.5 M potassium nitrate solution, 25.0 ml of ethanol, and 10.0 ml of a 0.2% gelatin solution; the solutions were mixed and 10.0 ml of 10^{-2} M lead nitrate solution added to each of the flasks. After 30 minutes polarograms were taken using a sensitivity of 1/50 (oxygen was removed beforehand from the solutions by means of a hydrogen stream).

* Translated from English by Z. I. Podgaiskaya.

The calibration curve is a straight line, at least up to a sulfate concentration of $1.75 \cdot 10^{-3}$ M. The break toward the end of the curve is explained by the solubility of the sulfate. From the slope of the linear section of the curve, taking into account that measurements of the polarographic wave of the lead ion can be carried out with an accuracy of 1%, the minimum amount of SO_4^{2-} ions which can be determined is $0.35 \cdot 10^{-3}$ M, the maximum experimental error being 5%. Results of sulfate ion determinations are given in the table.



Calibration curve.

Determination of Sulfate Ions in Water. The method described can be used for the determination of sulfate ions in water. Water, before or after purification, usually contains certain ions which interfere with the precipitation of sulfate ions by lead nitrate in the presence of ethanol; these ions include, e.g., calcium, trivalent iron, chloride, and carbonate ions. The ions indicated can be readily removed by passing the test solution through a column of cation exchange resin, and evaporating the solution obtained, after adding nitric acid and potassium nitrate to it. Addition of nitric acid ensures removal of hydrochloric acid. Potassium sulfate is converted into the sulfate which then serves as the supporting electrolyte.

Determination of Sulfate

SO_4^{2-} taken, mg	SO_4^{2-} found, mg	Error, %
2.40	2.45	+2.1
	2.36	−1.7
	2.43	+1.2
4.80	4.75	−1.0
	4.75	−1.0
	4.85	+1.0
7.20	7.15	−0.7
	7.17	−0.4
	7.28	+1.1

A description of the method developed for the determination of sulfate in water is given below. The requisite amount of test water is passed through a column packed with the cation exchange resin Amberlite-120 (in the H-form) at the rate of 0.01-0.05 ml/min per ml volume of the cation exchange resin. Fifty ml of the solution which has passed through the column is pipetted into a porcelain basin, and 0.5 ml of concentrated nitric acid and 5 ml of 0.1 M potassium nitrate added; the solution is evaporated to dryness on an electric steam bath. The residue is cooled and 10.00 ml of a 0.04% gelatin solution, 5.00 ml of ethanol, and 5.00 ml of 0.004 M lead nitrate solution added. The solution is transferred to the polarographic cell, oxygen is removed with a hydrogen stream, and polarograms taken at a sensitivity of 1/50. A calibration curve is constructed using known amounts of sulfuric acid.

The calibration curve is a straight line up to a concentration of 34 μg SO_4^{2-}/ml.

The method has been used for determining sulfate ions in purified water obtained from Porte Alegre (Brazil) tap water, containing 18.9 μg SO_4^{2-}/ml. The following values were found: 18.7, 19.1, 18.6, and 19.0 μg SO_4^{2-}/ml (the relative error is respectively 1.1, 1.1, 1.6, and 0.5% SO_4^{2-}).

SUMMARY

An indirect method for the polarographic determination of sulfate is described; it is based on precipitation of sulfate with lead nitrate in an aqueous-alcoholic medium containing 25% ethanol, followed by polarographic determination of excess lead ions. The method has given satisfactory results during the determination of sulfate in water. The water samples are previously freed from interfering ions by passing them through a cation exchange resin, and then evaporating the solutions obtained from the column with nitric acid to eliminate volatile acids, and with potassium nitrate in order to retain the sulfuric acid as sulfate.

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MICRODETERMINATION OF CARBONYL GROUPS BY AN OXIMATION METHOD

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Oximation with hydroxylamine hydrochloride has been in use for a long time for the quantitative macrodetermination of carbonyl groups [1]; $RCOR_1 + NH_2OH \cdot HCl \rightarrow RC(=NOH)R_1 + H_2O + HCl$. In the majority of methods, based on this reaction, which have been suggested, the carbonyl group content is determined on the basis of the amount of hydrochloric acid liberated. Several methods have been described for the macrodetermination of aldehydes and ketones, in which it is suggested that the oximation reaction be carried out in the presence of an organic base, e.g., pyridine [2], N-diethylaminoethanol [3], and octadecenylamine [4].

The micromethod which we should like to suggest for the determination of carbonyl groups is based on oximation with hydroxylamine hydrochloride in the presence of triethanolamine; the latter neutralizes the hydrochloric acid liberated and shifts the equilibrium toward quantitative formation of the oxime. Excess triethanolamine is determined visually or potentiometrically by titration with hydrochloric acid.

Oximation of carbonyl compounds proceeds via an addition stage:

$$(R)(R_1)CO + NH_2OH \rightleftarrows (R)(R_1)C(OH)(NHOH)$$
$$(R)(R_1)C(OH)(NHOH) \rightarrow (R)(R_1)C{:}NOH + H_2O.$$

The first, slow stage of the reaction which consists of an addition to the carbonyl group represents an attack on the carbon of the carbonyl group by a nucleophilic reagent:

$$>\overset{\delta\oplus}{C}=\overset{\delta\ominus}{O} + A^- \longrightarrow >C\begin{matrix}O^-\\ \diagdown\\ A\end{matrix}$$

and accordingly, the reactivity of the carbonyl group should depend to a marked extent on the value of the positive charge on the carbonyl carbon atom. The greater the positive charge the easier the oximation reaction.

In this connection, oximation of aldehydes with a 0.1 N alcoholic solution of hydroxylamine hydrochloride proceeds very rapidly, even at room temperature. The rate at which ketones are oximated depends markedly on their structure and on the nature of the radicals connected to the carbonyl group. Ketones which have two methylene groups alongside the carbonyl group (i.e., of the type $-CH_2-CO-CH_2-$) are also oximated very rapidly. Ketones which have a methyl group alongside the carbonyl group react more rapidly than ketones which have another alkyl group alongside the carbonyl group; this can be explained by the large inductive effect of higher alkyl radicals, and by an increase in steric hindrance. Taking as an example the oximation of 4,7-dimethyldecanone-5, it is clear how important is the position of the carbonyl group in the ketone molecule (Table 2). On the other hand, an electron-withdrawing group should increase the positive charge of the

carbon atom. Thus, p-nitroacetophenone is oximated considerably more readily than acetophenone. Ketones which have a tertiary or quaternary carbon atom alongside the carbonyl group, react fairly slowly. The oximation rate decreases strongly in the case of compounds of the type $>CH-CO-CH<$ or $\rangle C-CO-CH<$ and in these cases it is usually necessary to heat with a 0.5 N solution of hydroxylamine hydrochloride.

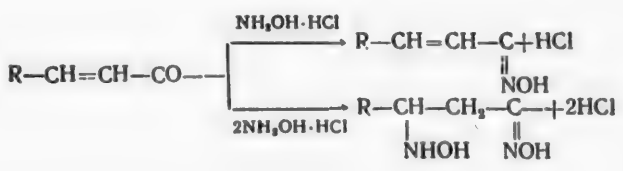
TABLE 1

Oximation at Room Temperature (0.7 g $NH_2OH \cdot HCl$ in 100 ml of reaction solution)

Test material	Sample wt.	Duration	CO, %		
			calculated	found	difference
Vanillin**	9.356	30 min	18.41	18.45	+0.04
Ditto	9.118	30 "	18.41	18.28	−0.13
Heliotropine**	7.500	30 "	18.66	18.82	+0.16
Ditto	7.455	30 "	18.66	18.68	+0.02
m-Nitrobenzaldehyde**	7.800	30 "	18.53	18.72	+0.19
Ditto	9.628	30 "	18.53	18.69	+0.16
Salicaldehyde**	7.653	30 "	22.94	22.85	−0.09
Ditto	10.418	30 "	22.94	23.16	+0.22
Citral**	4.357	30 "	18.40	18.22	−0.18
Ditto	4.735	30 "	18.40	18.11	−0.29
Methyl ethyl ketone	4.863	30 "	38.85	38.67	−0.18
Ditto	4.622	30 "	38.85	38.55	−0.30
Pinacoline*	5.363	1 hr	27.97	27.74	−0.23
Ditto	5.176	1 "	27.97	27.80	−0.17
2,3-Dimethylheptene-2-one-6**	9.723	30 min	19.98	19.94	−0.04
Ditto	9.505	30 "	19.98	19.84	−0.14
2,6-Dimethylundecanone-10**	6.862	30 "	14.12	14.00	−0.12
Ditto	5.227	30 "	14.12	14.09	−0.03
Phenylacetone**	6.432	30 "	20.88	20.64	−0.24
Ditto	6.205	30 "	20.88	20.58	−0.30
Cyclohexanone**	4.432	30 "	28.54	28.63	+0.09
Ditto	5.058	30 "	28.54	28.52	−0.02
Trans-α-decalone**	4.185	30 "	18.40	18.48	+0.08
Ditto	4.185	30 "	18.40	18.62	+0.22
p-Nitroacetophenone**	8.285	2 hrs	16.96	17.09	+0.13
Ditto	7.847	2 "	16.96	16.87	−0.09
Acetoacetic ester*	6.185	30 min	21.52	21.48	−0.04
Ditto	7.625	30 "	21.52	21.47	−0.05
Ethyl ether of 4-oxo-2-pentene-1-carboxylic acid**	5.160	30 "	17.93	17.95	+0.02
	7.063	30 "	17.93	17.83	−0.10
1,4-Dimethyl-2-keto-cyclopentane-5-carboxylic acid*	6.690	2 hrs	17.93	17.82	−0.11
	7.515	2 "	17.93	17.64	−0.29

* Visual titration; ** visual titration with addition of sodium chloride.

It has been established [5] that unsaturated ketones which have a system of crossed double bonds (of the type $-CH=CH-CO-CH=CH-$), in contrast to unsaturated ketones with a single double bond (of the type $-CH=CH-CO-$) or diarylketones, are capable of adding on hydroxylamine along the double bond. Such ketones can simultaneously react in two ways, with formation of the oxime of the ketone and the oxime of the hydroxyaminoketone:



The carbonyl content of such ketones cannot be determined by the method suggested.

The suggested method has been used for determining the carbonyl content of various classes of organic compounds: aldehydes, aldoses, ketones, keto acid esters, and also diketones and quinones capable of giving dioximes.

TABLE 2

Oximation at 70-75°

Test material	Sample wt.	$NH_2OH \cdot HCl$ in 100 ml of reaction solution, g	Duration of heating, hr	CO, %		
				calc.	found	difference
Galactose*	9.307	0.7	1	15.55	15.25	—0.30
Ditto	7.636	0.7	1	15.55	15.39	—0.16
Glucose*	6.240	0.7	1	14.13	14.25	+0.12
Ditto	5.780	0.7	1	14.13	14.43	+0.30
Acetophenone*	6.017	0.7	1	23.31	23.55	+0.24
Ditto	7.150	0.7	1	23.31	23.19	—0.12
Carvone*	5.427	0.7	1	18.65	18.57	—0.08
Ditto	5.549	0.7	1	18.65	18.39	—0.26
Benzoin**	9.210	0.7	1	13.20	13.24	+0.04
Ditto	8.816	0.7	1	13.20	13.30	+0.10
3(p-methoxyphenyl)2-cyclohexenone-1**	7.983	0.7	1	13.85	13.80	—0.05
	8.580	0.7	1	13.85	13.73	—0.12
2,2-Tetramethylene-5,5-dimethyltetrahydrofuranone-3*	6.930	0.7	1	16.65	16.71	+0.06
	5.599	0.7	1	16.65	16.42	—0.23
2,2-Pentamethylenehexahydrochromanone-4***	7.535	0.7	1	12.60	12.44	—0.16
	9.909	0.7	1	12.60	12.60	0.00
Methyl-α-thienylketone*	4.830	0.7	2	22.20	22.06	—0.14
Ditto	5.222	0.7	2	22.20	22.11	—0.09
Diisopropylketone*	4.185	0.7	3	24.53	24.34	—0.19
Ditto	5.887	0.7	3	24.53	24.24	—0.29
Benzophenone*	7.095	3.5	2	15.37	15.78	+0.41
Ditto	8.146	3.5	2	15.37	15.37	0.00
4,7-Dimethyldecanone-5***	6.626	3.5	3	15.20	15.15	—0.05
Ditto	6.069	3.5	3	15.20	15.49	+0.29
Dimedone*	3.476	0.7	1	39.96	39.94	—0.02
Ditto	4.799	0.7	1	39.96	39.83	—0.13
3-Methoxy-Δ^9-isoestrachryzanenedione-15. 17a***	7.550	0.7	1	18.90	18.87	—0.03
	7.526	0.7	1	18.90	18.81	—0.09
2-Phenylindanedione-1,3***	4.454	3.5	1	25.21	25.65	+0.44
Ditto	4.358	3.5	1	25.21	25.43	+0.22
2,2,6,6-Tetramethyltetrahydropyranedione-3,5***	4.167	3.5	2	32.91	32.74	—0.17
	3.980	3.5	2	32.91	32.92	+0.01
Benzoquinone, 1,4***	2.600	0.7	3	51.83	51.80	—0.03
Ditto	2.570	0.7	3	51.83	51.54	—0.29
α-Naphthoquinone***	3.085	0.7	3	35.42	35.28	—0.14
Ditto	3.080	0.7	3	35.42	35.12	—0.30
1,4-Dimethy-2-ketobicyclo-[2,2,1]-heptane-5-carboxylic acid*	8.219	0.7	2	15.37	15.15	—0.22
	8.190	0.7	2	15.37	15.07	—0.30
2,7-Dimethyl-3-ketobicyclo-[2,2,1]-heptane-5,6-dicarboxylic acid*	8.269	3.5	4	12.38	12.13	—0.25
	9.365	3.5	4	12.38	11.89	—0.49

* Visual titration; ** visual titration with addition of sodium chloride;
*** potentiometric titration.

During attempts to determine the carbonyl group in keto acids and also in the presence of organic acids which do not dissociate strongly, it was established that it is necessary to titrate the reaction solution with hydrochloric acid to a lower pH value than is necessary during determination of other classes of carbonyl compounds; otherwise, high results were obtained during determination of the carbonyl group content. The method described cannot be used for the determination of a carbonyl compound in the presence of organic acids which dissociate strongly.

Experimental. The reaction solution is prepared as follows: 0.7 g (or 3.5 g for preparation of a 0.5 N solution) of hydroxylamine hydrochloride is dissolved in 10 ml of water, 0.5 g of triethanolamine is added, the volume is then made up to 100 ml with 96% ethanol. The indicator is prepared by dissolving 0.1 g of bromophenol blue in 100 ml of 20% ethanol.

Experimental Procedure. Into a 100 ml conical flask with a ground glass stopper is introduced from a buret 5 ml of the reaction solution; an aliquot of test material (3-10 mg) is then added to the flask. Depending on the structure of the test material, the flask is allowed to stand for 0.5-2 hours at room temperature, or a ground glass air condenser is connected to the flask and the latter heated on a water bath at 70-75° for 1-4 hours. A control test is carried out in the same way. When oximation is carried out on heating, on completion of the reaction, the flask is cooled to room temperature. Excess triethanolamine is titrated with 0.02 N hydrochloric visually or potentiometrically.

When a visual indication of the end point is used, three drops of the indicator solution is added in the control experiment, the solution is then titrated with hydrochloric acid until a bluish-green color is obtained (to a lemon-yellow color in the case of determination of carbonyl groups in a keto acid or in the presence of an organic acid). The solution in the flask containing the aliquot of test material is titrated in the same way. In order to compare the color of the solutions in the control and in the test itself, before completing the titration of the test solution, to the latter is added a volume of distilled water which is approximately equal to the difference between the volume of hydrochloric acid used up in titrating the control (a ml) and in titrating the test solution; after addition of the requisite amount of distilled water, titration is continued until the same color as that obtained in the control is reached (b ml).

TABLE 3

Determination of Carbonyl Groups in the Presence of Acids* (0.7 g $NH_2OH \cdot HCl$ in 100 ml of reaction solution)

Test material	Sample wt.	Temp.	Duration of reaction	CO, %		
				calc.	found	difference
Vanillin Benzoic acid	6.804 2.200	Room	30 min	13.91	13.84	—0.07
Vanillin Benzoic acid	6.175 3.348	"	30 "	11.94	12.15	+0.21
Acetophenone Acetic acid	4.141 1.845	70—75°	1 hr	16.13	16.01	—0.12
Acetophenone Acetic acid	3.820 1.665	70—75°	1 "	16.23	16.12	—0.11
Cyclohexanone Adipic acid	7.633 2.705	Room	30 min	21.07	21.02	—0.05
Cyclohexanone Adipic acid	4.065 4.922	"	30 "	12.91	12.94	+0.03
Dimedone Succinic acid	4.668 2.240	70—75°	1 hr	27.00	26.91	—0.09
Dimedone Succinic acid	3.110 3.476	70—75°	1 "	18.87	18.67	—0.20

* Visual titration.

Since the pH of distilled water is considerably higher than the pH of the solution on completion of titration, the amount of hydrochloric acid required to titrate 20 ml of water in the presence of three drops of indicator solution is determined in a separate experiment; on the basis of this experiment a correction (c ml)* is calculated for the amount of water added to the flask containing the test aliquot. Titration is carried out in diffused daylight in flasks made of the same type of glass. When 2 ml of a saturated aqueous solution of sodium chloride is added to the contents of the flasks before starting a titration, a more even titration end point is obtained.

The carbonyl group content is calculated by means of the formula:

$$CO,\ \% = \frac{28.01 \cdot N \cdot (a - b + c) \cdot 100}{m},$$

where N is the normality of the hydrochloric acid and m is the weight of the aliquot in mg.

During potentiometric titration, titration is first carried out visually using an indicator until the greenish-yellow color of the latter is reached (to a pH of about 3.3), the solution is then transferred to a beaker and titrated potentiometrically to a pH of 3.3 using glass and calomel electrodes.

The necessity of the preliminary visual titration is explained by the fact that it is inconvenient to titrate potentiometrically at once in a flask, and, moreover, since the solution being titrated will have a pH within 3.3-3.5 (the volume of the solution at this stage is 10-13 ml) any loss incurred in transferring the solution to a beaker has very little effect on the experimental results.

The carbonyl group content on carrying out a potentiometric titration is calculated by means of the formula:

$$CO,\ \% = \frac{28.01 \cdot N\,(a - b) \cdot 100}{m},$$

where N is the normality of the hydrochloric acid; a is the volume of hydrochloric acid used in titrating the control, ml; b is the volume of hydrochloric acid used in titrating the test solution; and m is the weight of aliquot, mg.

Potentiometric titration is recommended in those cases where the solution to be titrated is colored, and also if it is turbid.

It has been found that when a 0.1 N solution of hydroxylamine hydrochloride is used the accuracy of the method is about ± 0.3%, while when a 0.5 N solution of hydroxylamine hydrochloride is used the accuracy of the method drops to ± 0.5%.

Tables 1-3 contain results of the analyses of carbonyl compounds by the suggested method.

SUMMARY

A method has been developed for the microdetermination of carbonyl compounds by oximation with hydroxylamine hydrochloride in the presence of triethanolamine. The method can be used for the determination of carbonyl groups in aldehydes, ketones, keto acids, keto acid esters, and also in diketones and quinones which can form dioximes.

It has been established that it is possible to determine carbonyl compounds in the presence of organic acids which only dissociate to a small extent.

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QUANTITATIVE DETERMINATION OF MONOSUBSTITUTED 1-, 3-, 4- OXADIAZOLES BY POTENTIOMETRIC TITRATION WITH SODIUM NITRITE

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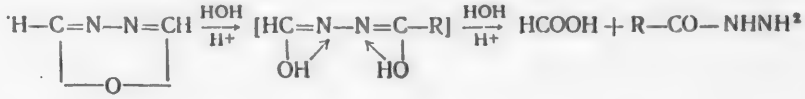
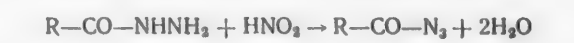
In recent years derivatives of 1-, 3-, 4-oxadiazole have found increasing application in pharmacy [1], in dye production [2], and in scintillation techniques [3]. Hitherto, as far as we are aware, however, no methods have been published on their quantitative determination. In this connection, therefore, we have developed a method for the quantitative determination of 2-substituted derivatives of 1-, 3-, 4-oxadiazole.

During a study of chemical reactions in the 1-, 3-, 4-oxadiazole series [4], it was found that monosubstituted derivatives of 1-, 3-, 4-oxadiazole readily interact with sodium nitrite even in the cold in aqueous solutions of mineral acids, to form reaction products which are sparingly soluble in this medium. In the course of a more detailed study of this reaction it was found that it proceeds in two stages. In the first stage, acid hydrolysis of the monosubstituted 1-, 3-, 4-oxadiazole to the corresponding primary hydrazide and formic acid occurs according to the following scheme:



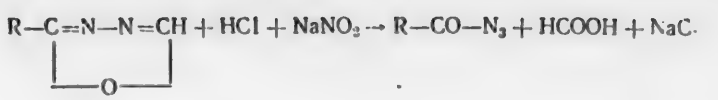
It was established that hydrolysis proceeds almost instantaneously – immediately after dissolving the test material in acid. Thus, we isolated the hydrolysis products of 2-phenyl-1-, 3-, 4-oxadiazole, and 2-(p-nitrophenyl)-1-, 3-, 4-oxadiazole, these proved to be identical in elemental composition and melting point with the corresponding benzhydrazide and p-nitrobenzhydrazide.

The second stage consists of the further interaction of the primary hydrazide with nitrous acid according to the well-established reaction with formation of the corresponding azide:



The precipitated azides were identified by means of their elemental composition, melting point, and other properties as well (their ready solubility in diethyl ether, their insolubility in water, their tendency to explode on melting). Thus, 2-phenyl-1-, 3-, 4-oxadiazole gave benzoylazide, while 2-(p-nitrophenyl)-1-, 3-, 4-oxadiazole gave p-nitrobenzoylazide, and 2-(p-tolyl)-1-, 3-, 4-oxadiazole gave p-tolylazide, etc.

Thus, the over-all interaction between monosubstituted derivatives of 1-, 3-, 4-oxadiazole with sodium nitrite in an acid medium can be expressed by the general equation:



As is clear from this equation monosubstituted derivatives of oxadiazole react under the given conditions with sodium nitrite in equimolar amounts. The reaction proceeds rapidly on the whole, and, as was demonstrated, it proceeds quantitatively, thanks to which it can be used for the potentiometric titration of 2-substituted derivatives of 1-, 3-, 4-oxadiazole.

The test materials which were used for the potentiometric work, and whose synthesis has been described [4, 5], were purified by vacuum distillation (low melting) until they gave constant absorption spectra, and by recrystallization or by passing through a chromatographic column; the treatment used depended on the individual properties of each test compound.

Measurements were carried out on the LP-5 tube potentiometer of the MOSKIP factory. A saturated calomel electrode was used as the null electrode, and a bright platinum electrode as the indicator electrode. The sodium nitrite solution was standardized potentiometrically against p-nitraniline and sulfanilic acid [6]. This solution was kept in a dark colored hermetically sealed flask. Titration was carried out from a buret, the drawn-out tip of which was immersed in the solution being titrated. During a determination, the sodium nitrite was initially added in large aliquots, while as the end point came nearer the aliquots of titrant added were decreased until their volume was equal to a half scale division on the buret.

An aliquot of test material was usually dissolved in concentrated hydrochloric acid which was subsequently diluted two-three times with distilled water. As control tests showed, the acid concentration does not affect the experimental accuracy essentially. It was found possible to titrate sparingly soluble oxadiazoles in a mixture of hydrochloric and glacial acetic acid with the preliminary heated solution of the test sample.

The potential was rapidly established at the beginning of titration, while toward the end it took 3-4 minutes to be established. Addition of KBr as a catalyst, a technique which has been successfully used for the potentiometric titration of aromatic amines [6], and of hydrazides as well [7], with sodium nitrite, was found to have almost no effect on the rate at which the potential was established in the given instance. During the first moments after addition of each new portion of titrant there was observed an instantaneous increase in the potential, this was followed by a gradual drop to a known established value; this is explained by an accumulation of NO_2^- ions in the first moments, as has been shown during the titration of amines [6, 8] and hydrazides [7]. The potential jump for the compounds which we examined lay within the range 640-730 mv, accordingly, the approach of the end point can always be observed.

The experimental accuracy is about 1% (see table).

Determination of Certain Oxadiazoles

1-, 3-, 4-Oxadiazole	Sample wt. mg	Found, %	Error, %
2-Phenyl-	46.6	100.3	0.3
2-(p-Nitrophenyl)-	32.8	101.1	1.1
2-(p-Tolyl)-	23.3	99.0	1.0
2-(p-Methoxyphenyl)-	23.4	99.2	0.8
2-(p-Aminophenyl)-	55.0	101.3	1.3
2-(p-Dimethylamino-phenyl)-	2.0	99.2	0.8
2-(p-Carbethoxy-phenyl)-	3.2	98.8	1.2

When the oxadiazole molecule contains a group which is also capable of quantitatively interacting with sodium nitrite, as in the case of 2-(p-aminophenyl)-1-, 3-, 4-oxadiazole, double the amount of sodium nitrite is used, as is the case during titration of aminobenzhydrazides [7].

Since good results are also obtained with amounts of test materials amounting to 10^{-5} mole, the method can be used both as a macro- and microvariant without modifying the method essentially.

Experimental Procedure. An aliquot (0.01-0.1 mM) of the monosubstituted 1-, 3-, 4-oxadiazole is dissolved in concentrated hydrochloric acid, and, in the case of readily soluble oxadiazoles, the solution is diluted with 2-3 times its amount of water. For the determination of sparingly soluble compounds, it is expedient to add some glacial acetic acid, or to heat the solution with the sample. Next, with vigorous stirring, large aliquots (0.5-1 ml) of titrant are added initially from a buret whose tip is immersed in the solution being titrated; the size of the aliquots of 0.01 N sodium nitrite is decreased (0.1-0.01 ml) as the end point is approached. The end point corresponds to the maximum increase in the potential $\Delta E/\Delta V$, where ΔE is the difference in mv between two successively added portionsd sodium nitrite, and ΔV is the volume of the portion of sodium nitrite added.

The reaction product – the corresponding aroylazide – which separated out during titration does not interfere with the determination.

The gram-equivalent of the monosubstituted 1-, 3-, 4-oxadiazole which is being titrated is numerically equal to its molecular weight.

SUMMARY

A method has been developed for the quantitative determination of monosubstituted 1-, 3-, 4-oxadiazoles in which the latter are potentiometrically titrated with sodium nitrite. The determination can be carried out on a macro as well as a micro scale. A study has been made of the chemical reactions of monosubstituted 1-, 3-, 4-oxadiazoles during their titration with sodium nitrite in an acid medium.

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DETERMINATION OF SUGARS BY DIRECT TITRATION WITH AN ALKALINE SOLUTION OF THE COPPER COMPLEX OF TRIHYDROXYGLUTARIC ACID

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Classical methods [1-3] of determining sugary materials use Fehling's solution, which consists of an alkaline solution of the copper complex of tartaric acid [4]. The main difficulty connected with the use of this solution is the fact that no proportionality is observed between the amount of cuprous oxide formed and the amount of sugary material in solution. We have described macro- [5] and micromethods [6] for the permanganometric determination of sugars by means of the copper complex of xylotrihydroxyglutaric acid. It was found that on replacing Fehling's solution by an alkaline solution of the copper complex of trihydroxyglutaric acid, under the conditions which we had established, there is a strict proportionality between the amount of sugar and the amount of cuprous oxide formed.

Direct titration of sugars is widely used in industry, although this method suffers from greater drawbacks than the permanganometric or gravimetric methods. In Soxhlet's first variant [1] Fehling's solution was heated in an open basin and the sugar solution added to it until complete reduction of cupric to cuprous was achieved. Heating the solution in a flask, which enables one to depress the reverse oxidation of cuprous oxide by atmospheric oxygen, and the use of external indicators (potassium ferrocyanide, sodium thiosulfate) significantly increase the accuracy of the method. The use of external indicators, however, demands that boiling be stopped and leads to expenditure of test liquid. This drawback was eliminated by Lane and Eynon [7] who added methylene blue as an internal indicator to the Fehling solution. In order to prevent overheating of the liquid and to prevent oxidation of cuprous oxide by atmospheric oxygen, it has been suggested that the sugar solution be added to the flask containing the Fehling solution, steam being passed through it continuously. When such a technique is used, separation of suspended cuprous oxide, which is bright-red in color, interferes considerably with the end point. It has been found that addition of potassium ferrocyanide to the Fehling solution eliminates separation of cuprous oxide [8-12].

Despite all these improvements, the direct titration method still has some disadvantages which are related to the nature of the Fehling solution itself. They reduce to the fact that the oxidation of the sugars cannot be subjected to stoichiometric calculations (Table 1). It is only possible to assume a more or less satisfactory inverse proportionality between the volume of solution containing the reducing sugars and its concentration, over a narrow concentration range. Accordingly, in the well-known methods of Lane and Eynon [7], and Nizovkin and Emel'yanova [11], etc., it is recommended that two operations always be carried out, from the first operation an approximate idea is obtained how much the solution should be diluted so that its concentration lies within this narrow range. When an alkaline solution of cupritrihydroxyglutarate is used there is no need for this operation. As can be seen from Table 1, there is a strict inverse proportionality between the volume of sugar solution used in the titration, and its concentration. Consequently, there is no need to carry out an approximate determination.

The present article contains results on the determination of pure monosaccharides: glucose, fructose, galactose, mannose, xylose, and, in addition, invert saccharose in solutions of varying concentration. This method permits sugar to be determined in fruits, fruit juices, wines, confectionary, pentose and hexose hydrolyzates, etc. A statistical treatment of the results has shown that the method has a high degree of accuracy in all cases.

TABLE 1

Sugar	Conc. of sugar solution g/liter	Amt. sugar soln. used for titrating 10 ml of Fehling's soln. ml (mean of 4 determinations)	For titrating 10 ml of cupritrihydroxyglutaric acid solution			Probable deviation of the mean result, $S_{\bar{x}}$
			no. of expts.	sugar solution used, ml	amt. of sugar used, mean value, mg	
Glucose	1.000	5.70	9	6.00— 6.10	6.05	0.0090
	0.500	5.79	9	12.05—12.15	6.05	0.0042
	0.333	5.84	9	18.10—18.20	6.05	0.0034
Fructose	1.000	5.90	4	6.20— 6.25	6.21	0.0126
	0.500	6.17	4	12.40—12.45	6.21	0.0072
	0.333	6.40	4	18.60—18.65	6.21	0.0040
Galactose	1.000	6.43	4	6.85— 6.90	6.89	0.0125
	0.500	6.59	4	13.75—13.80	6.89	0.0063
	0.333	7.04	4	20.65—20.70	6.89	0.0049
Mannose	1.000	5.88	4	6.30— 6.35	6.34	0.0127
	0.500	6.06	4	12.65—12.70	6.34	0.0063
	0.333	6.19	4	19.00—19.05	6.34	0.0049
Invert saccharose	1.000	5.60	9	5.80— 5.85	5.84	0.0074
	0.500	5.68	4	11.65—11.70	5.84	0.0072
	0.333	5.80	4	17.50—17.55	5.84	0.0049
Xylose	1.000	5.67	9	6.05— 6.15	6.10	0.0118
	0.500	5.75	9	12.15—12.25	6.10	0.0042
	0.333	5.96	9	18.25—18.30	6.10	0.0019

The following solutions are used for the determination.

Solution No. 1. 10.000 g of $CuSO_4 \cdot 5H_2O$ (chemically pure grade recrystallized from water) is accurately weighed out and dissolved in water, 0.04 g of methylene blue is added. The volume of the solution is accurately made up to one liter.

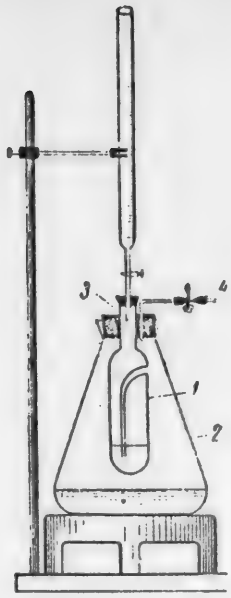
Solution No. 2. 32 g of trihydroxyglutaric acid,* 90 g of sodium hydroxide, and 4 g of potassium ferrocyanide — $K_4[Fe(CN)_6] \cdot 3H_2O$ are dissolved in water and the volume made up to one liter. If the solution thus prepared is not clear enough, it is filtered through a No. 3 glass crucible or through glass wool.

By pouring together equal volumes of these two solutions an alkaline solution of cupritrihydroxyglutaric acid is obtained.

Analytical Procedure. Determinations were carried out in the apparatus shown in the diagram, this can be replaced by an even simpler homemade apparatus [13].

Five ml each of solution No. 1 and solution No. 2 are introduced into the inner vessel. At the same time 250-300 ml of water are heated to the boil in vessel 2. When the water in the flask is boiling, the inner flask with the solution of the copper complex is fitted into it mounted in a stopper. When vessel 1 has heated up enough, steam starts to pass through the solution and causes it to boil evenly. Excess steam from the inner vessel passes out through 3 in the neck of vessel 1. Clip 4 is used for regulating the pressure inside the conical flask 2.

* Acid, "for foodstuffs" grade produced by the hydrolysis industry [6] can be used.



1) Inner vessel; 2) outer vessel; 3) exit for steam from the inner vessel; 4) rubber valve with clip.

When the solution of the copper complex starts to boil, the liquid whose sugar content it is desired to determine is added from the buret at the rate of 3-4 drops per second until the blue color of the liquid in the inner flask turns violet. Starting at this point, one waits for two minutes and then continues to titrate at the rate of one drop per 5-6 seconds (not quicker) until there is a sharp change from violet to a weak-yellow which indicates the end point. A determination normally takes 4-5 minutes.

Determination of Glucose and Other Monosaccharides. Chemically pure grade sugar which had been dried beforehand to constant weight at 40-60° was used. Titration was carried out from a buret whose scale divisions had an accuracy of 0.02 ml. The standard vessel was calibrated with water.

The experimental results are given in Table 1.

Determination of Sugary Materials in Industrial Products by the Method of Additions. Samples of industrial products were prepared according to published instructions [11, 14, 15, 16]. The content of sugary material was calculated by means of the formula: $x = k/V$ mg/ml, where V is the number of ml of sugar solution used up in the titration, while k is the titer of 10 ml of copper complex solution; k for the various sugars has, under the operational conditions indicated above, the values given in Table 1; for glucose e.g., the value is 6.05.

Table 2 contains the sugar content expressed as mg per g of solid product (e.g., apples, caramel), or in mg per ml of liquid product (juice, wine).

TABLE 2

Product tested	Sugar added	One liter of solution contained: technical product	One liter of solution contained: added sugar (g)	Ml of soln. used for titrating 10 ml of the copper complex	Sugar found (mean value) in mg/g of product (or mg/ml respectively)	Dispersion	Accuracy	Probable relative error, %
"Kal'vil' White Winter" apples	glucose	2.000 g	0	24.90—24.95	121.4	0.02	0.2	0.16
			0.250	12.25—12.30	121.2	0.25	0.8	0.3
			0.500	8.13— 8.15	121.4	0.23	0.8	0.2
"Rkatsiteli" grape juice	glucose	5.00 ml	0	6.40—6.45	188.3	0.7	1.4	0.7
			0.250	5.05—5.10	188.5	1.6	2.0	0.8
			0.500	4.15—4.20	189.0	2.9	2.7	0.9
"Muscat Moldavain Desert wine	invert saccharose	5.00 ml	0	7.90—8.00	146.9	0 6	1.2	0.8
			0.250	5.90—5.95	146.7	0.7	1.3	0.7
			0.500	4.70—4.75	147.1	2.3	2.4	1.0
"Teatral'naya" caramel	glucose	4.000 g	0	7.10—7.15	212.0	0.5	1.2	0.5
			0.250	5.50—5.55	211.9	1.6	2.0	0.7
			0.500	4.45—4.50	212.1	3.1	2.8	0.8
"Vesna" confectionary	invert saccharose	2.000 g	0	4.55—4.60	638.3	14	6.0	0.9
			0.250	3.80—3.85	638.5	33	9.2	1.2
			0.500	3.25—3.30	638.4	46	10.7	1.2
Corn stalks (pentose hydrolyzate)	xylose	2.500 g	0	6.40—6.45	379.0	2.2	2.4	0.6
			0.250	5.10—5.15	377.2	5.8	3.8	0.8
			0.500	4.20—4.25	379.2	11.6	5.4	0.9
Corn stalks (hexose hydrolyzate)	glucose	2.500 g	0	8.30—8.35	290.3	0.8	1.4	0.5
			0.250	6.20—6.25	289.6	2.4	2.5	0.6
			0.500	4.90—4.95	290.4	5.8	3.8	0.6

These results are the mean of four determinations. When the method of additions was used, the amount of sugar added was subtracted from the sugar content found by titration.

The mean square error of a single determination (dispersion)

$$s^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1},$$

is also given where n is the number of determinations; the accuracy of the method calculated by the formula:

$$h = t_a \cdot s_{\bar{x}}$$

is given for α (confidence) = 0.95. Here $s_{\bar{x}} = \frac{s}{\sqrt{n}}$ is the probable deviation of the mean result.

The probable relative error is given in %:

$$\frac{s_{\bar{x}} \cdot t_{0.95}}{a} \cdot 100$$

In most cases the probable relative error does not exceed 1%.

SUMMARY

A new method is suggested for the direct titration of sugary materials by means of an alkaline solution of the copper complex of trihydroxyglutaric acid. It has been established that, in contrast to methods based on the use of Fehling's solution, there is a strict inverse proportionality between the volume of solution used up in a titration and its concentration.

It has been shown that the method can be used for the determination of sugary materials in fruits, fruit juices, wines, confectionary, pentose and hexose hydrolyzates with a high degree of accuracy.

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QUANTITATIVE DETERMINATION OF IMPURITIES IN ADIPONITRILE

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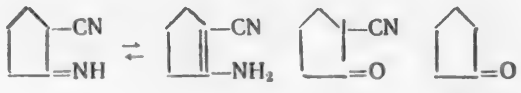
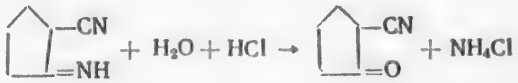
One of the intermediate products during the production of polyamide resins is adiponitrile (the dinitrile of adipic acid). In order to obtain high quality polyamide resins, only minimum amounts of impurities can be permitted in the adiponitrile. In a previous paper [1] it was shown that the main impurities in adiponitrile are 1-imino-2-cyanocyclopentane or 1-amino-2-cyanocyclopentene-1,2 (I), 2-cyanocyclopentanone-1 (II), and cyclopentanone (III).



I II III

There are no published methods for the quantitative determination of impurities in adiponitrile. Indirect methods have been used for getting an indication of the purity of adiponitrile: setting point, color, permanganate number, acidity, etc. [1].

We have developed a method for the quantitative determination of impurities in adiponitrile. The basis of the method is an acidimetric determination of 1-imino-2-cyanocyclopentane (I), and a polarographic determination of 2-cyanocyclopentanone (II) and cyclopentanone (III). The cyanimine is not reduced on a dropping mercury electrode. Its determination is based on the fact that its molecule contains the readily hydrolyzed imine group. Hydrolysis is effected with weak hydrochloric acid:



The cyanoimine (I) content of the adiponitrile is determined by back titrating the excess hydrochloric acid. Using the Chugaev-Zerewitinov method the amount of active hydrogen in the cyanoketone was found to be the theoretical value. It follows from this that the cyanoketone (II) enolizes readily. It is also possible that the equilibrium between the keto- and enol-forms in this compound is shifted toward the latter. In II the nitrile group is conjugated with the double bond. It is known [2] that such compounds are reduced on a dropping mercury electrode. Experiments showed that 2-cyanocyclopentanone-1 (II) is actually reduced at $E_{1/2} = -2.0$ v with respect to the saturated calomel electrode (S.C.E.). Cyclopentanone (III), like other ketones [3] is reduced at a very negative potential $E_{1/2} = -2.6$ v (S.C.E.)., and this strongly complicates its determination. At high cyclopentanone concentrations in the liquid which is being polarographed (about 0.06%) a maximum appeared which we were unable to suppress. The half-wave potentials of the cyanoketone (II) and cyclopentanone (III) differ strongly from each other (Fig. 1). This means that it is possible to determine the cyanoketone (II) and cyclopentanone (III) quantitatively in each others presence.

The electrical reduction of 2-cyanocyclopentanone-1 (II) and cyclopentanone (III) was studied on a M-8 type polarograph of Gor'ky University. The galvanometer sensitivity was $2.79 \cdot 10^{-9}$ amp/mm, while the capillary characteristic was $m^{2/3} \cdot t^{1/6} = 1.384$ mg$^{2/3}$ sec$^{-1/2}$. All the tests were made at 25 ± 0.3°. Adiponitrile which had been purified by the sulfuric acid-permanganate method [4] followed by an additional treatment with ammonium bisulfite, was used for the work. Twice distilled isopropanol was used. The test compounds were synthesized by methods published previously [1].

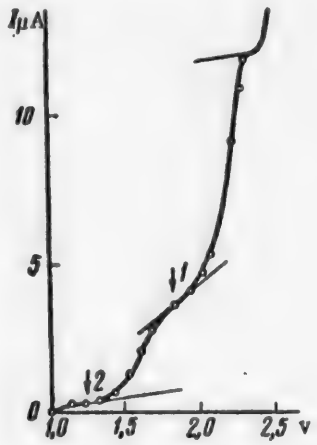


Fig. 1. Polarograms for a 0.042% solution of cyclopentanone (1) and a 0.025% solution of 2-cyanocyclopentanone-1 (2) in a supporting electrolyte of 0.1 N tetraethylammonium iodide solution.

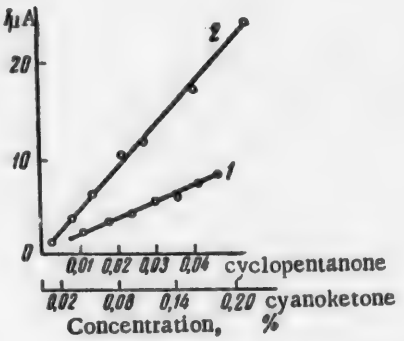


Fig. 2. Calibration lines for cyclopentanone (1) and 2-cyanocyclopentanone-1 (2).

The solution in which the reduction of the cyanoketone (II) and cyclopentanone (III) on a dropping mercury electrode was studied, contained 40% of adiponitrile and 35% of isopropanol. This enabled down to 0.005% of impurity to be determined. The isopropanol served for homogenizing the adiponitrile and the aqueous solution of the supporting electrolyte. Tetraethylammonium iodide at a concentration of 0.1 N in the solution being polarographed was used as the supporting electrolyte. From the fact that the ratio I_d/C (Table 1) is constant for the concentration range studied, it follows that the wave heights for cyanoketone (II) and cyclopentanone (III) are proportional to their concentrations.

TABLE 1

2-Cyanocyclopentanone-1 (II)		Cyclopentanone (III)		2-Cyanocyclopentanone-1 (II)		Cyclopentanone (III)	
Concentration, %	I_d/C	Concentration, %	I_d/C	Concentration, %	I_d/C	Concentration %	I_d/C
0.011	107	0.012	179	0.086	116	0.030	180
0.032	113	0.018	174	0.108	113	0.041	173
0.054	110	0.024	179	0.216	109	0.046	176

Experiments were carried out within the concentration ranges (in the solution being polarographed) 0.005-0.22% for the cyanoketone (II) and 0.01-0.06% for cyclopentanone (III).

The possibility of simultaneously determining 2-cyanocyclopentanone (II) and cyclopentanone (III) was checked within the concentration ranges indicated above. It was found that the ratio of the concentrations, in percent, for the cyanoketone (II) and cyclopentanone (III) should not be greater than 1 : 2. In this case, the wave height for cyclopentanone (III) does not depend on the presence of (II). The presence of cyclopentanone

(III) in any concentrations does not affect the value of the limiting current of the cyanoketone (II). Adiponitrile and 1-imino-2-cyanocyclopentanone (I) do not change the values of the limiting current for the cyanoketone (II) and cyclopentanone (III) over a wide concentration range.

Method for Determination of Cyanoimine (I), Cyanoketone (II), and Cyclopentanone (III). In order to determine 1-imino-2-cyanocyclopentane an aliquot of adiponitrile (about 10 g) is placed in a 100 ml conical flask. Fifteen ml of isopropanol and 20-25 ml of water are added. Five ml of a 0.005 N HCl is added with a pipet and the solution well mixed by shaking. Excess HCl is then titrated with 0.005 N NaOH using bromothymol blue as indicator. The 1-imino-2-cyanocyclopentane content (in %) is calculated by means of the formula:

$$\frac{108\,(V_1K_1-V_2K_2)N\cdot 100}{q\cdot 1000},$$

where 108 is the mol. wt. of 1-imino-2-cyanocyclopentane; V_1 is the volume of 0.005 N HCl taken for hydrolysis; V_2 is the volume of 0.005 N NaOH used in the titration; N is the normality of the acid and alkali; K_1 and K_2 are corrections for the acid and alkali titers; q is the weight of the aliquot taken in g.

To determine the cyanoketone (II) and cyclopentanone (III), 10 ml of adiponitrile is placed in a 25 ml standard flask. To this flask is added by means of a pipet 5 ml of a 0.5 M aqueous solution of tetraethylammonium iodide and 7 ml of isopropanol. The contents of the flask are carefully mixed and made up to the mark with water. The solution to be polarographed is swept with nitrogen for 15 minutes. Polarograms are taken with a capillary with a slow drop rate, the anode is a mercury pool. The minimum concentrations of the impurities which can be determined in adiponitrile by the method developed are as follows: the cyanoimine (I) – 0.001%; the cyanoketone (II) – 0.008%; and cyclopentanone (III) – 0.01%. A determination does not take longer than 40 minutes. The content of the cyanoketone (II) and cyclopentanone (III) is determined by means of calibration lines constructed beforehand (Fig. 2). The method was checked by analyzing a series of synthetic mixtures (Table 2).

TABLE 2

Cyanoimine (I), %			Cyanoketone (II), %			Cyclopentanone (III), %		
taken	found	deviation	taken	found	deviation	taken	found	deviation
0.022	0.023	+0.001	0.021	0.019	—0.002	0.041	0.041	—
0.015	0.014	—0.001	0.015	0.016	+0.001	0.033	0.032	—0.001
0.011	0.011	—	0.012	0.012	—	0.028	0.027	—0.001
0.0022	0.0022	—	0.010	0.010	—	0.024	0.024	—
0.0011	0.0010	—0.0001	0.003	0.003	—	0.021	0.019	—0.002

The method developed has been used for the analysis of samples of adiponitrile purified by various methods.

SUMMARY

The conditions for the reduction of 2-cyanocyclopentanone-1 and cyclopentanone on a dropping mercury electrode have been studied.

A method has been developed for the simultaneous quantitative determination of 1-imino-2-cyanocyclopentane, 2-cyanocyclopentanone-1, and cyclopentanone in adiponitrile.

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COPRECIPITATION OF TUNGSTEN WITH FERRIC HYDROXIDE

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It has been indicated in the literature that it should be possible to coprecipitate small amounts of tungstate ions with ferric hydroxide [1-3]. In some cases the coprecipitation has been regarded as complete [1], while in other cases it has been indicated that only 70-79% of the tungsten is coprecipitated [3]. There is no published information on the relation between completeness of coprecipitation of tungsten and the various conditions under which the process is carried out.

Coprecipitation of tungstate ions with ferric hydroxide was studied with the aid of the radioactive isotope W^{185}. The distribution of tungsten between the solution and precipitate was determined on the basis of the radioactivity of the dry residue obtained after evaporating part of the solution (0.200 ml) in a platinum basin; the radioactivity was measured with a T-25 BFL torsion counter on a B-2 setup. The precipitate was separated from the solution of centrifugation, while the pH of the solution was measured with two glass electrodes on a LP-5 pH-meter. The ionic strength of the solution containing ammonium chloride amounted to 0.2, 1.0, and 2.0 in individual series of experiments. The time for which the solution was in contact with the precipitate was 30 minutes, as a rule. The volume of the solution was 20.0 ml, while the temperature was 18°.

It is known [4-6] that when natural tungsten is bombarded with neutrons, in addition to W^{185}, the long life W^{188} isotope ($T_{1/2}$ = 65 days) may be obtained as a result of the successive capture of two neutrons by the W^{186} isotope; the W^{188} isotope, as a result of β-decay, then gives the rhenium isotope Re^{188} which possesses very hard β- and γ-radiation. It has been shown earlier [7] that the insignificant amount of the Re^{188} isotope present as an impurity in W^{185}, can lead, under certain conditions of measuring the activity of the W^{185} – such that conditions may arise which cause a large absorption of the soft β-radiation of W^{185} – to some distortion of the results when the behavior of tungsten is controlled on the basis of the W^{185} isotope. It has also been shown that results of a photometric determination of tungsten in solution by the thiocyanate method do not always completely coincide with the results of radiometric determinations of tungsten in the same solution, probably, because the change in color of the thiocyanate complex of tungsten with time is not recorded sufficiently accurately, although the absence of a definite limiting amount of tungsten in solution can be observed by this method.

Bearing in mind what has been said above, the activity of E^{185} was measured at a minimum distance of the precipitate from the counter window (8 mm), and at an original activity of the preparation of 1800-2600 cpm. The standard and the test sample were always dried at the same temperature (96°) and in the course of the same time, while the salt composition of the standard and test solution was also the same. Under these conditions the experimental error arising from the presence of Re^{188} was less than 0.5%; this was determined on the basis of the absorption of the radiation by aluminum and on the basis of the activity of the solution after complete coprecipitation of tungstate ions with ferric hydroxide. Completeness of coprecipitation in a series of experiments was controlled by photometric determination of tungsten in solution (thiocyanate method) as well as by measurement of the radioactivity of the solution.

From the measurements of the radioactivity of solutions by various methods it was found that in the pH range starting with the pH at which coagulation of the precipitate starts, to pH 7.7, coprecipitation of tungstate ions with ferric hydroxide proceeds quantitatively, when the activity was measured with a T-25 BFL counter under the conditions indicated above (Curve 1, Fig. 1). When the MST-17 counter was used, and the distance between the counter window and the sample, and the amount of salt in solution increased, it was necessary to increase the amount of radioactive tungsten added to the potassium tungstate, while at the same time the fraction of Re^{188} in solution increased, and this led to an increase in the difference between the actual value of the coprecipitation (100%) and that measured to 6% (Curves 2 and 3).

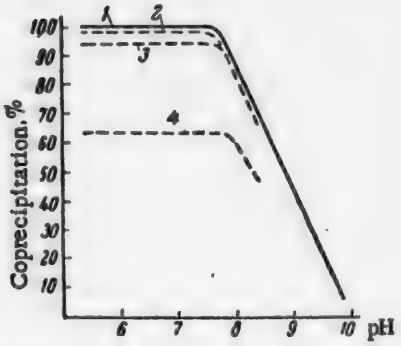

Fig. 1. The apparent value of the coprecipitation of tungstate ions with ferric hydroxide, as a function of the conditions used for measuring the activity.

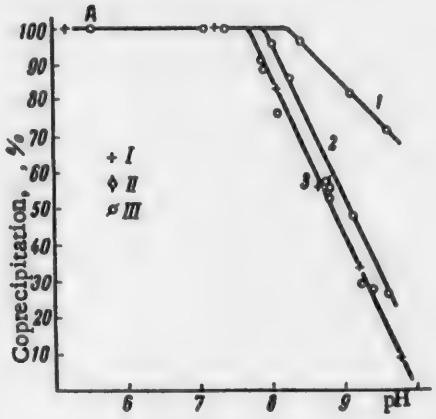

Fig. 2. Coprecipitation of tungsten with ferric hydroxide when the various solutions are added in different orders, and for variations in the ammonium salt concentration. W = 1 mg; Fe = 0.1 mg-atom; $[NH_4Cl]$ = 1 M; T = 30 min; I) W = = 100 μg; $[NH_4Cl]$ = 0.2 M; II) $[NH_4Cl]$ = = 0.2 M; III) $[NH_4Cl]$ = 2 M; 1) $Fe(OH)_3$ precipitated in the presence of K_2WO_4; 2) $FeCl_3$ added to a mixture of K_2WO_4 and NH_4Cl solutions; 3) K_2WO_4 added to freshly precipitated $Fe(OH)_3$.

On measuring the activity of the solution in a glass cuvette with an AS-1 counter, this difference can be as much as 40% (Curve 4). The technique indicated above for measuring the W^{185} activity almost excludes the effect of Re^{188}, present as an impurity, on the experimental results.

Coprecipitation of tungstate ions with ferric hydroxide in an alkaline medium depends on the pH of the medium and also on the order in which the solutions are poured together (Fig. 2). Coprecipitation, which is a maximum on precipitating ferric hydroxide in the presence of tungstate ions (Curve 1), decreases on precipitating the carrier by pouring ferric chloride into an alkaline solution containing tungstate (Curve 2), and is at a minimum on adding potassium tungstate to freshly precipitated ferric hydroxide. In all the cases indicated the time for which the precipitate was in contact with the solution was 30 minutes.

Thus, coprecipitation and 1 mg of tungsten (and 100 μg W, Curve 3) is quantitative in the pH range starting from the pH at which coagulation of the precipitated commences, to pH 7.7-8.2. Tungsten is also completely coprecipitated when the carrier is precipitated with pyridine (point A). Changes in the ammonium chloride concentration from 0.2 to 2.0 M do not affect the extent to which tungsten is coprecipitated with ferric hydroxide, which testifies to the chemosorptive nature of the coprecipitation of tungstate ions with ferric hydroxide, this is presumably related to the formation of sparingly soluble tungstates on the surface of the hydroxide precipitate. Some authors have shown that, at a pH less than 7, various forms of the tungstate ions may be present in solution, including polymeric tungstate ions. Independently of the composition and charge of these ions, their coprecipitation with ferric hydroxide is complete over a wide pH range. WO_4^{2-} ions are found in the alkaline region, this is confirmed, in our opinion, by the slope of Curve 1, Fig. 2, and the slope of similar coprecipitation curves for SO_4^{2-}, HPO_4^{2-}, CrO_4^{2-}, MoO_4^{2-} ions with ferric hydroxide under identical conditions.

Sorption of tungstate ions by the surface of the ferric hydroxide precipitate on adding potassium tungstate to freshly precipitated ferric hydroxide, increases with an increase in the time for which the precipitate is in contact with the solution (Fig. 3). During adsorption of chromate ions by ferric hydroxide, maximum coprecipitation is reached in the course of the first minute [7]; with time there occurs a slow decrease in adsorption, presumably, as a result of the crystallization of the carrier precipitate. In similar experiments on the coprecipitation of tungstate ions with ferric hydroxide, there is at first a rapid, and then a slow absorption of tungstate ions by the carrier precipitate. Maximum sorption is achieved in the course of the first 10-15 hours for which the solution is in contact with the precipitate (Curve 3); the percentage sorption does not change in the course of the subsequent 30-50 hours.

Vikt. I. Spitsyn [8] has shown that on decreasing the pH of the medium to 8-6, the tungstate ions are converted into paratungstate ions. Under our conditions (pH 8-10) this process, probably, does not occur in solution, nevertheless, the increase in the sorption of tungstate ions by the negatively charged precipitate of ferric hydroxide in the pH range indicated testifies to the occurrence of a chemical process which leads to an increase in coprecipitation of tungsten. Such processes could be: the slow penetration of tungsten ions right into the hydroxide precipitate with formation of iron tungstates; the formation in solution, or on the precipitate surface, of aquopolyanions of tungsten. The first of the processes indicated is the least likely, since experiments have shown that about 10-15% of chromate ions coprecipitated with ferric hydroxide, on precipitation of the carrier in the presence of the anion, cannot be extracted from the precipitate without dissolving the carrier, since the diffusion processes within the ferric hydroxide micelles, apparently, proceed very slowly.

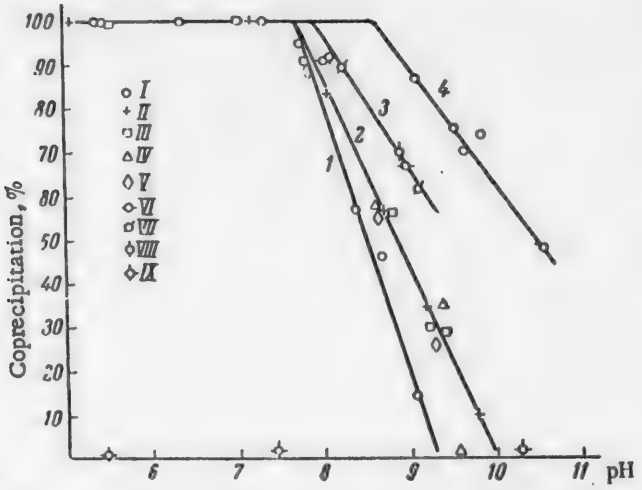

Fig. 3. Effect of time on the coprecipitation of tungstate ions with ferric hydroxide. W = 1 mg; Fe = 0.1 mg-atom; [NH_4Cl] = 1 M; 1) 2 min; 2) 30 minutes - 2 hours; 3) 15-45 hours; 4) coprecipitation of 1 mg W with ferric hydroxide (0.2 mg-atom Fe); T = 30 min; I) 1-2 min. (Curve 1); II) 30 min; 100 μg W; III) 30 min; IV) 1 hr; V) 2 hr; VI) 15 hrs; VII) 22 hrs; VIII) 45 hrs; IX) 1 μg Re; 30 min.

Thus, bearing in mind Spitsyn's views on the formation of aquopolyanions, which depend to a considerable extent on a tendency to hydrogen bond formation on the part of the acid anions, which is characteristic for aquopolytungstates, one can postulate the following chemistry of the process for the increase in sorption of tungstate ions by ferric hydroxide with time: initially, the tungstate ions are sorbed by the surface of the hydroxide precipitate, sorption being realized by means of the hydrogen bond formed with the hydrogen atoms of the hydroxyl groups of the hydroxide. Subsequently, the sorbed tungstate ions can, at the expense of the water hydrogen ions which are necessary for forming new hydrogen bonds, combine with new tungstate anions, and

this leads to an increase in sorption as a result of some polymerization (probably, di- or trimerization, since coprecipitation does not increase more than 2-3 times with the course of time) of tungstate ions on the surface of the hydroxide precipitate. Apparently, this process of polymerization on the precipitate surface occurs at higher pH values of the medium than in solution, as a result of the formation of a hydrogen bond between precipitate and anion. The presence of ammonium salts in solution gives rise to buffer properties in the medium. When a considerable amount of alkali is added to the solution, the tungsten sorbed by the precipitate goes into solution, which testifies to the surface character of the process.

On increasing the amount of carrier to 0.2 mg-atoms of iron, coprecipitation of tungstate ions, on precipitating ferric hydroxide in their presence, increases (Curve 4); the pH region within which complete coprecipitation of 1 mg of tungsten occurs increases to 8.6. Coprecipitation of perrhenate ions (1 μg Re) under the same conditions, in the presence of 1 mg of tungsten, hardly occurs at all, the behavior of the rhenium under these conditions is controlled by means of the radioactive isotope Re^{186}. This difference in the extent to which tungsten and rhenium are coprecipitated with ferric hydroxide in the pH range 5-8 can be used for the separation of these elements, the rhenium remains in solution, while the tungsten is completely precipitated.

SUMMARY

Tungstate ions are coprecipitated with ferric hydroxide quantitatively in the pH range covering the pH at which coagulation of the precipitate occurs, to pH 7.5-8.5; on increasing the pH further, coprecipitation decreases.

Coprecipitation of tungstate ions with ferric hydroxide is independent of ammonium chloride concentration, and increases with the time for which the precipitate is in contact with the solution.

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DETECTION OF SOME DIVALENT CATIONS BY MEANS OF β-HYDROXYNAPHTHALDEHYDE

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β-Hydroxynaphthaldehyde can be used for the quantitative determination of magnesium, copper, and beryllium [1-3]. Further studies have established that during the interaction of divalent cations with the aldehyde indicated in an alcoholic-aqueous-ammoniacal medium, imine compounds are not formed, but the complexes

$$(C_{11}H_7O_2)_2Me^{2+} \quad \text{or} \quad (C_{11}H_7O_2)_2Me^{2+} \cdot xH_2O \text{ [4]}.$$

are obtained.

The present article is devoted to the conditions necessary for obtaining characteristic crystalline precipitates of copper, beryllium, zinc, strontium, calcium, cobalt, and nickel ions with β-hydroxynaphthaldehyde, and to methods which have been developed for the qualitative detection of certain metals in mixtures and alloys.

Detection of Certain Cations. Copper. To 0.5 ml of the heated test solution is added 1 ml of a 2% alcoholic solution of β-hydroxynaphthaldehyde, two drops of 1 N sodium hydroxide is then added, light-yellow prismatic, needle-like – sometimes rhombic – crystals collected in sheafs immediately appear. The refractive index is 1.64; the crystals exhibit considerable pleochroism with strengthening of the yellow light. The limit of identification is 32 μg/ml; the limiting dilution is 1:32,000.

Beryllium. To 0.5 ml of test solution is added the same volume of a 2% solution of the aldehyde. The mixture is heated to the boil, and then one drop of 1 N sodium hydroxide is added; short, acicular, prismatic crystals are obtained, which sometimes have vertical shadings, they form characteristic ferny or branch-like aggregates colored a greenish-yellow color. The crystals belong to the hexagonal syngony and possess insignificant pleochroism with an increase in the greenish-yellow tone. The refractive index is 1.58-1.60. The limit of identification is 8 μg/ml; the limiting concentration is 1:128,000.

Other cations are detected like copper and beryllium.

Magnesium. From hot solutions, yellow, prismatic, pinacoidal, crystals separate out, and also acicular, star-like aggregates. The crystals possess a weak pleochromism of a yellowish color; the refractive index is 1.52-1.59. The limit of identification is 15 μg/ml; the limiting concentration is 1:64,000.

Calcium. Calcium separates out from cold solutions in the form of fine, light-yellow prisms with longitudinal shading. The crystals exhibit weak pleochroism with an increase or a decrease in the weak yellow color. The refractive index is 1.55-1.56. The limit of identification is 8 μg/ml; the limiting concentration is 1:128,000.

Strontium separates out almost immediately from cold solutions at a concentration of 1 mg/ml in the form of fine, long needles of a weak-yellow color collected into bundles. From more dilute solutions a precipitate settles out after 5 minutes. The pleochroism is weak with a small increase in the yellow color. The reaction has a low sensitivity.

Zinc, after adding to a hot mixture of equal volumes of a zinc salt and the aldehyde, two drops of 1 N sodium hydroxide, separates out in the form of weak greenish, columnar, acicular prism, which often collect

* Deceased.

in nodules. The pleochroism is weak with an increase in the yellow light, extinction angle 45°. The limit of detection is 32 μg/ml; the limiting concentration is 1 : 32,000.

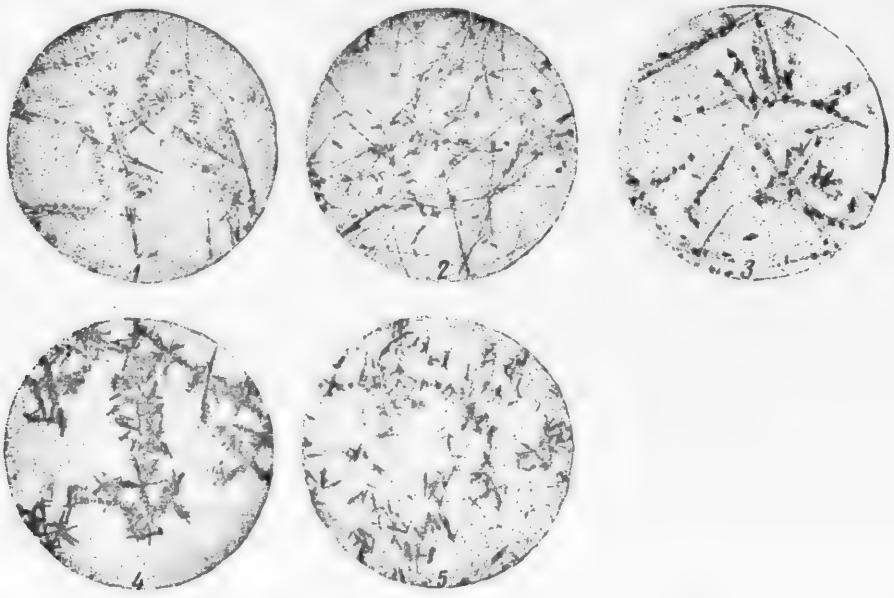
Manganese separates out from cold solutions after addition of β-hydroxynaphthaldehyde and one drop of 1 N sodium hydroxide. On shaking there are formed weak-yellow, fine, acicular crystals collected in ray-like and star-like formations. The pleochroism is weak and yellow in color. The refractive index is 1.65. The limit of identification is 32 μg/ml; the limiting concentration is 1 : 32,000.

Cobalt and Nickel give, from hot solutions, on addition of the aldehyde and one drop of sodium hydroxide, almost identical greenish-yellow, prismatic crystals, gathered in star-like and radial ray-like aggregates. The pleochroism is weak with an increase in the lemon-yellow color. The refractive index is 1.58-1.60. The limit of identification is 16 μg/ml; the limiting dilution is 1 : 64,000.

Analysis of Mixtures of Certain Cations. Magnesium and calcium can be detected in the presence of strontium in weakly alkaline solutions. In the cold there are formed crystals of the compounds of β-hydroxy-naphthaldehyde with calcium and magnesium cations which can be distinguished by differences in their form.

The limiting ratios are as follows: Sr : Ca = 6 : 1 (Fig. 1); Sr : Mg = 2.6 : 1 (Fig. 2).

Beryllium can also be detected in the presence of copper on the basis of the formation of crystals which are characteristic for each of them taken separately. The limiting ratio is Cu : Be = 5 : 1 (Fig. 3).



Figs. 1-5.

Detection of Beryllium in Bronze and Steels. 0.25 g of bronze containing about 2% beryllium is dissolved on heating in 5 ml of 1 N nitric acid, the solution is then diluted with water to 100 ml. To 1 ml of this solution, which contains about 0.05 mg Be/ml, is added four drops of a 10% solution of sodium ethylenediaminetetracetate until a blue color appears, 1.5 ml of a 2% alcoholic solution of the aldehyde is then added, and, after heating, a few drops (about 4) of 1 N sodium hydroxide is added until an emerald-green color appears. On shaking, a precipitate of the beryllium compound separates out (Fig. 4). The minimum beryllium concentration that can be detected is 25 μ g/ml. Beryllium can be detected in the same way in steels (Fig. 5).

SUMMARY

Crystalloscopic methods have been developed for the detection of Ca^{2+}, Be^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+} and other divalent metals by means of β-hydroxynaphthaldehyde in an alcoholic-alkaline medium. Crystalline precipitates are obtained at pH 7.5-8.

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MICRODETERMINATION OF COPPER IN ORGANIC COMPOUNDS BY COMBUSTION IN OXYGEN

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In recent years the attention of analysts has been drawn to Schoniger's method which permits determination of a number of elements in nonvolatile organic compounds. An aliquot of test material is wrapped up in filter paper, the latter is wound with platinum wire, and the paper is burnt in a flask filled with oxygen. The method has been successfully used for the determination of halogens [1], sulfur [2], and phosphorus [3]. It is obvious that it could also be used for the analysis of the organic complex compounds of a number of metals. In this article we shall describe a technique for the analysis of inner complex compounds of copper.

An aliquot of test material containing 4-5 mg is weighed out on a microbalance, in a glass tube with a long tip, and it is strewn onto the middle of an ashless filter paper. The filter is folded up in such a fashion as to leave a free end, and is fitted to the end of a platinum wire fused into a flask as indicated in Schoniger's method [1, 2].

Twenty ml of 0.5 N sulfuric acid is poured into a 500 ml conical flask and oxygen passed into the flask for several seconds from a cylinder. The free end of the filter paper is ignited and is immediately introduced into the flask, the stopper is held in position in the flask by hand for the first few seconds otherwise it will be blown out. Combustion is complete in a few seconds. The flask is then shaken and a few drops of water introduced along the glass stopper into the flask which is then allowed to stand for 15-20 minutes. The tap is opened and the stopper removed and rinsed with water. The solution is transfered from the flask into a 100 ml conical flask and is heated to the boil. The platinum wire is heated for several seconds in the oxidizing flame of a

* Original Russian pagination. See C. B. translation.

burner in order to oxidize any small amounts of metallic copper which may have been formed, the wire is then lowered into the flask containing the solution and the latter boiled for 1-2 minutes. When all the cupric oxide has dissolved, the wire is rinsed with water, and the solution evaporated to a volume of 15 ml.

To the cooled solution is added 25% ammonia until a weak blue color appears, 5 ml of 50% acetic acid solution is then added followed by about 1 g of potassium iodide; the liberated iodine is titrated with 0.02 N sodium thiosulfate until a weak yellow color is obtained, 1 ml of a 1% starch solution is added and titration continued until the color changes from blue-brown to white-rose.

The experimental error is ± 0.2%. A determination takes about 30 minutes. Results of some determinations are given in the table.

Test material	Sample wt.	Copper content, %		
		found	calc.	difference
Copper salicylal	23.091	20.83	20.73	+0.10
$C_{14}H_{10}O_4Cu$	22.919	20.61		—0.18
Copper salicylalmethylamine	24.259	19.35	19.15	+0.20
$C_{16}H_{16}O_2N_2Cu$	24.919	19.28		+0.13
Copper salicylalimine	27.438	21.00	20.90	+0.10
$C_{14}H_{12}O_2N_2Cu$	27.010	20.88		—0.02
Cu salt of β-hydroxynaphthaldehyde	23.832	15.63	15.65	—0.02
$C_{22}H_{14}O_4Cu$	23.450	15.77		+0.12
Cu salt of benzoylacetone	14.537	16.44	16.37	+0.07
$C_{20}H_{20}O_4Cu$	18.114	16.32		—0.04
Copper salt of benzoylacetaldehyde	19.253	17.65	17.78	—0.13
$C_{18}H_{14}O_4Cu$	17.388	17.85		+0.07

SUMMARY

A rapid method has been developed for the determination of copper in organic compounds, it is based on combustion in a flask filled with oxygen, with subsequent iodometric titration of the copper. The error is ± 0.2%.

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SPECTROPHOTOMETRIC TITRATION OF ERBIUM WITH SODIUM ETHYLENEDIAMINETETRACETATE (EDTA-Na) IN THE PRESENCE OF PYRIDYL-(2-AZO-4)-RESORCINOL

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The rare earths form colored complex compounds with pyridyl-(2-azo-4)-resorcinol (PAR) in neutral or weakly alkaline media. In Fig. 1 are shown absorption curves of the complex compound of erbium with PAR (Curve 1), and of a solution of the indicator itself (Curve 2). They show that it should be possible to titrate erbium spectrophotometrically using PAR as an indicator at the absorption maximum of 504 mμ. Titration at the absorption maximum of the indicator at 415 mμ is impossible because of the appreciable absorption of the compound of erbium with PAR. Sodium ethylenediaminetetracetate (EDTA-Na) was used as the titrant. It is clear from Fig. 2 that maximum absorption of solutions of the compound of erbium with PAR occurs at pH 8.0-8.8.

Spectrophotometric titration of erbium with EDTA-Na solution using PAR as indicator is carried out at 504 mμ and a pH of 8.5, using a SF-4 instrument and a cuvette of optical glass with a capacity of 25 ml. The EDTA-Na solution is added from a 2 ml microburet, and

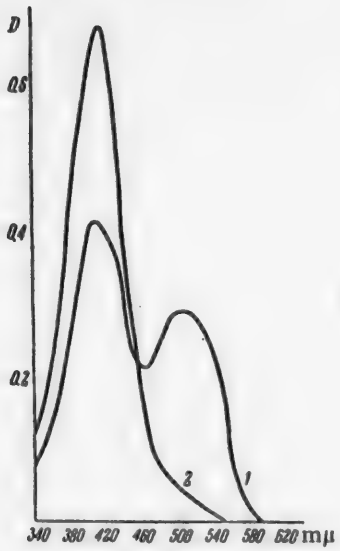

Fig. 1. Absorption curves: 1) 1×10^{-3} M solution of the compound of erbium with pyridyl-(2-azo-4)-resorcinol; 2) 2×10^{-3} M solution of pyridyl-(2-azo-4)-resorcinol; pH 8.5.

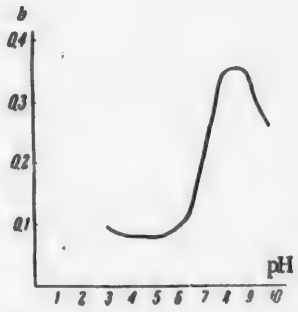

Fig. 2. The relation between the optical density of solutions of the compound of erbium with pyridyl-(2-azo-4)-resorcinol and pH.

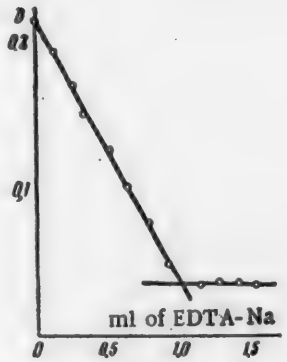

Fig. 3. Titration of an erbium salt with EDTA-Na in the presence of pyridyl-(2-azo-4)-resorcinol.

is stirred with a glass stirrer, for this purpose the metal lid of the spectrophotometer is replaced by a bakelite lid with two holes.

For titration, to the cuvette containing 10 ml of an acetate-ammoniacal buffer with pH 8.5 is added 0.3 ml of a 2×10^{-3} M aqueous solution of PAR, various amounts of erbium, and the solution diluted to 20 ml. The end point on titrating with a 5×10^{-3} M solution of EDTA-Na is determined by the intersection point of two straight lines (Fig. 3).

Results of titration of erbium with EDTA-Na in the presence of PAR (Table) confirm the possibility of determining total rare earths (on the basis of erbium titration) by indicator spectrophotometric titration, with an error which does not exceed the limits of the possibility of this method. The possibility of determining the rare earths with PAR is determined by the high sensitivity of the reaction with the indicated reagent (for erbium the sensitivity of the reaction is 0.2 $\mu g/ml$; the molar absorption coefficient $\epsilon = 46{,}000$). The method permits determination of 10^{-4} - 10^{-3} g of the rare earth element.

There is a possibility that the rare earths can be determined in the presence of thorium at pH 8.5.

Er taken, mg	Amt. of EDTA-Na solution used, ml	Er found, mg	Error	
			mg	%
0.334	0.39	0.326	—0.008	—2.4
0.502	0.64	0.535	+0.033	+6.6
0.836	0.98	0.819	—0.017	—2.0
0.836	0.98	0.819	—0.017	—2.0

SUMMARY

A method has been developed which is suitable for the determination of 10^{-3} to 10^{-4} g of erbium and the total rare earths. The experimental error is 3-4%.

A NEW TITRIMETRIC METHOD OF DETERMINING RHENIUM IN ALLOYS

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Titrimetric methods of determining rhenium are not numerous. The method of reducing septivalent rhenium with zinc, followed by titration with solutions of oxidizing agents [1, 2], have not found practical application because of the poor reproducibility of the results obtained. Reduction of perrhenate by a bismuth amalgam has been used by Lazarev [3] for the quantitative determination of rhenium in solutions free from foreign impurities. We have developed a titrimetric method for the determination of rhenium which is based on the quantitative reduction of septivalent rhenium to the quadrivalent state by means of a standard solution of a divalent chromium salt [4].

In trying to find the effect of small amounts of molybdenum on the determination of rhenium by the method of chromometric titration [4], the optimum conditions were established (acidity, temperature). When the amount of molybdenum present is a few times greater than the amount of rhenium, most of the molybdenum should be removed by an extraction method [5-12], chromatographically [13-14], or by distillation [15]. Iron, titanium, chromium, vanadium, niobium, copper, and manganese can be readily removed by precipitating them with ammonia or alkali.

As a result of our work we have developed a technique for the determination of rhenium in alloys of varying composition (Table).

Composition of the alloy	Rhenium found, %		
	by thiocyanate method and by spectrophotometric meas. of perrhenate in alkaline region	by titration with $CrSO_4$	
		parallel determinations	Mean
Re, Ni (77.0), Mn (0.5), Fe (21.0)	1.0	0.96; 0.99	1.0
Re, Mo (0.57), Ni (69.0), Mn (0.5), Cu (28.0), Ti (2.0)	1.5	1.51; 1.51	1.5
Re, Co (51.0), Fe (38.0)*	10.40	10.00; 10.24	10.1
Re, Co (51.0), Fe (42.0)	5.90	6.17	6.2
Re, Fe	3.0	2.98	3.0
Re, Cr, Al, Ni	3.5	3.38; 3.48	3.4
Re, Cr, Al, Fe	11.0	10.90	10.9
Re, Ti, Ni, Fe	2.5	2.32; 2.32; 2.53	2.4
Re, Ni	7.10	7.04	7.0
Re, Cr, (20.0), Fe (70.0), Al, V (3.3)	not determined	1.56; 1.63; 1.45	1.5
Re, Mo (0.3), Cr, Fe, V	Ditto	0.98; 0.88	0.9
Re, Mo (5.5), Ni, Cr, Fe**		13.45; 13.40; 12.95	13.3

* The titration curve is shown in Fig. 1.

** The titration curve is shown in Fig. 2.

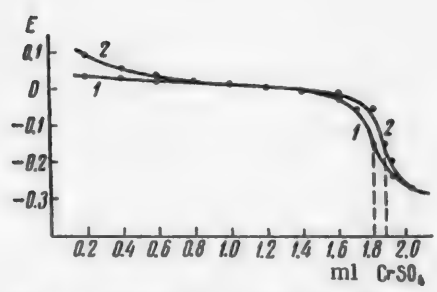

Fig. 1. Titration of septivalent rhenium with $CrSO_4$ in alloys containing cobalt and iron. 0.510 g of alloy; total V = = 50 ml; 1) 0.0895 N $CrSO_4$; V_{CrSO_4} = = 1.80 ml; V_{Re} = 10 ml; Found 10.00% Re; 2) V_{Re} = 10 ml; 0.0885 N $CrSO_4$; V_{CrSO_4} = 1.86 ml; Found 10.24% Re.

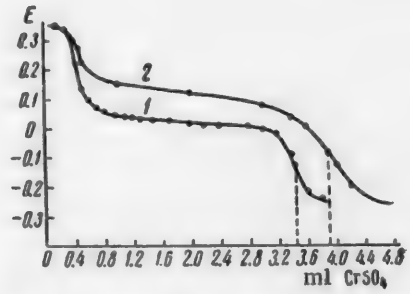

Fig. 2. Titration of septivalent rhenium with $CrSO_4$ in alloys containing Ni, Cr, Fe, and Mo (5.5%). 1) 0.5009 g of alloy; total V = 50 ml; 0.0720 N $CrSO_4$; $2V_{Re}$ = 10 ml; V_{CrSO_4} = 3.44-0.44 = = 3.00 ml; Found 13.40% Re; 2) 0.05005 g of alloy; total V = 50 ml; 0.0634 N $CrSO_4$; V_{Re} = 10 ml $CrSO_4$ = 3.90-0.48 ml = 3.42 ml; found 13.45%.

Reagents and Apparatus. A solution of a divalent chromium salt was prepared by A. I. Busev's method [16], while its concentration was determined by titration with $CuSO_4$ in HCl 1:1 [17]. The $CuSO_4$ was standardized electrolytically. Titration with the $CrSO_4$ solution was carried out in a small thermostatted cell [18] in an atmosphere of purified nitrogen. The potentials were measured by a compensation method on a Leeds and Northrup potentiometer. The indicator electrode was a platinum disc 0.2 x 1 cm, fused into a glass tube. The reference electrode was a saturated calomel electrode.

Titration Procedure. 0.5 g of alloy is dissolved in a mixture of hydrochloric and nitric acids (5 ml of concentrated HNO_3 + 5 ml of concentrated HCl) on heating. After the alloys had dissolved completely, the solution is evaporated on a water bath. To the 2-3 ml of residue is added a small amount of water and 2 ml of concentrated H_2SO_4, and the evaporation repeated on a water bath. In order to remove nitric acid completely

the evaporation is completed on a moderate hot plate until thick white fumes of SO_3 appear. By observing this condition there is almost no loss of rhenium.

The salt residue is dissolved on heating in 50 ml of water; the usual operation of precipitation with ammonia (for alloys containing Cr, V, Ti, and Fe) or alkali (for alloys containing Co, Ni, and Cu) [19] is then carried out from a hot 5% solution. The filtrates are evaporated to a small volume, and acid is added until the solution gives a neutral reaction with litmus paper; concentrated H_2SO_4 is finally added until its concentration in the solution is 5-6 N (7 ml of concentrated H_2SO_4 for 50 ml of the final volume).

Aliquots of 5, 10, or 20 ml of the solution are taken for titration, the amount taken being dependent on the rhenium content. The solution is placed in a special titration cell [18] through which is passed a stream of purified nitrogen. The cell is heated to 80° by means of a thermostat. KI crystals (about 1 mg) are added as a catalyst for the reduction of rhenium. The $CrSO_4$ solution is added from a 10 ml microburet. The potential of the platinum indicator electrode is measured on the potentiometer (as the potential jump approaches, the solution should be added dropwise).

When molybdenum is present, titration is carried out to the second potential jump on the platinum indicator electrode. The difference in the volumes of $CrSO_4$ solution used between the second and first potential jumps corresponds to the amount of $CrSO_4$ used for titrating the rhenium.

SUMMARY

A titrimetric method has been developed for the determination of rhenium; it is based on quantitative reduction of Re^{VII} to Re^{IV} by means of a solution of a divalent chromium salt, the titration end point being controlled potentiometrically. The method has been checked on alloys containing nickel, cobalt, chromium, iron, vanadium, titanium, copper, manganese, and molybdenum.

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MICROCRYSTALLOSCOPIC DETECTION OF SULFUR-CONTAINING ANIONS

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There are no satisfactory methods for the microcrystalloscopic detection of the anions SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ [1, 2]. The tetrathiourea salt of platinum $[Pt(SCN_2H_4)_4]Cl_2$,* obtained by Kurnakov [3] can be successfully used for detecting these anions.

This compound forms sparingly soluble characteristic crystals with the anions indicated.

The SO_4^{2-} ion, independently of the cation, gives $[Pt(SCN_2H_4)_4]SO_4$. The sulfate ion cannot penetrate into the inner sphere of the complex.

On mixing drops of the test solution containing SO_4^{2-} ions with a drop of the reagent solution, crystals are formed in the form of characteristic crosses (Fig. 1). Crystals in the form of fern leaves collected in the

Fig. 1

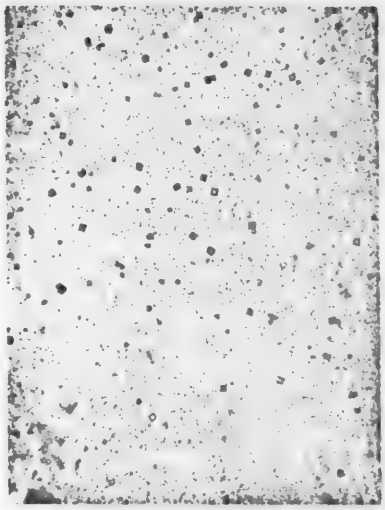

Fig. 2

* A compound with this composition can be readily prepared from potassium chloroplatinite and thiourea. In order that the salt obtained be free from foreign impurities it is best to prepare it in two stages. First of all, solutions of potassium chloroplatinite and thiourea are mixed in the molar ratio of 1 : 2 at room temperature. Platinum dichlorodithiourea $[Pt(SCN_2H_4)_2Cl_2]$ is precipitated. The precipitate is filtered off and washed free from potassium chloride. To one mole of the precipitate separated in this way is then added a further two moles of thiourea at 50-70°. During this stage the precipitate dissolves to form $[Pt(SCN_2H_4)_4]Cl_2$.

On careful evaporation there separates out a crystalline material which is bright-yellow in color and which is readily soluble in water. The salt obtained is used for microcrystalloscopic detection in the form of an aqueous solution whose concentration is 10-15 mg/ml.

form of a cross are obtained when the concentration of sulfate ions is high enough (up to 0.02 M). In the case of comparatively dilute solutions containing sulfate ions, square plates with a cross along the diagonals (Fig. 2) can be seen under the microscope. These crystals, under higher magnification prove to be the same sort of crystals as in the first instance but are not so developed. The limiting SO_4^{2-} concentration is 0.0002 M.

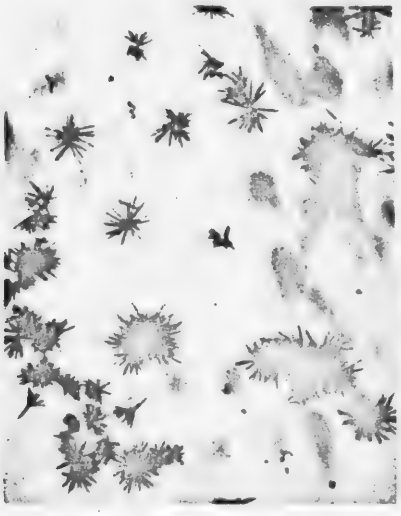

Fig. 3

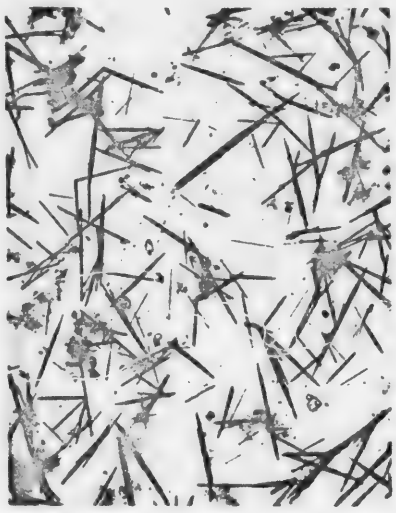

Fig. 4

Fig. 5

Sulfite ions interact with the reagent to form $[Pt(SCN_2H_4)_3SO_3]$.

Under ordinary conditions, the sulfite ion replaces only one molecule of thiourea in the inner sphere of the complex compound [4]. The compound formed in this case crystallizes in the form of fine needles collected into spheres (Fig. 3) which are yellowish in color. The reaction permits detection of SO_3^{2-} ions in 0.002 M solutions.

During the interaction of $S_2O_3^{2-}$ ions, the compound $[Pt(SCN_2H_4)_3S_2O_3]$ is formed. The platinum is connected with the sulfite ion through sulfur in the quadrivalent state, while the platinum is connected with the thiosulfate ion through the external atom of divalent sulfur.

A sparingly soluble compound in the form of long prisms, yellow in color, is formed with $S_2O_3^{2-}$ ions.

Further substitution of thiourea molecules in the inner sphere of the complex by $S_2O_3^{2-}$ ions may occur, with formation of two compounds containing a greater number of thiosulfate residues in their composition [5]. Accordingly, high concentrations of the thiosulfate solutions must be avoided (0.05-0.001 M with respect to thiosulfate). At higher thiosulfate concentrations a bright-yellow crystalline precipitate separates out (Fig. 5).

On adding a solution containing a mixture of SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ to a solution of the reagent, it is possible to detect all three ions. It is possible to detect relatively small amounts of SO_3^{2-} and $S_2O_3^{2-}$ ions in the presence of large amounts of SO_4^{2-} ions.

SUMMARY

The reagent $[Pt(SCN_2H_4)H_4]Cl_2$ forms sparingly soluble salts with characteristic crystalline forms with SO_3^{2-}, $S_2O_3^{2-}$, and SO_4^{2-} ions. This reaction permits the detection of these ions even when they are present together.

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